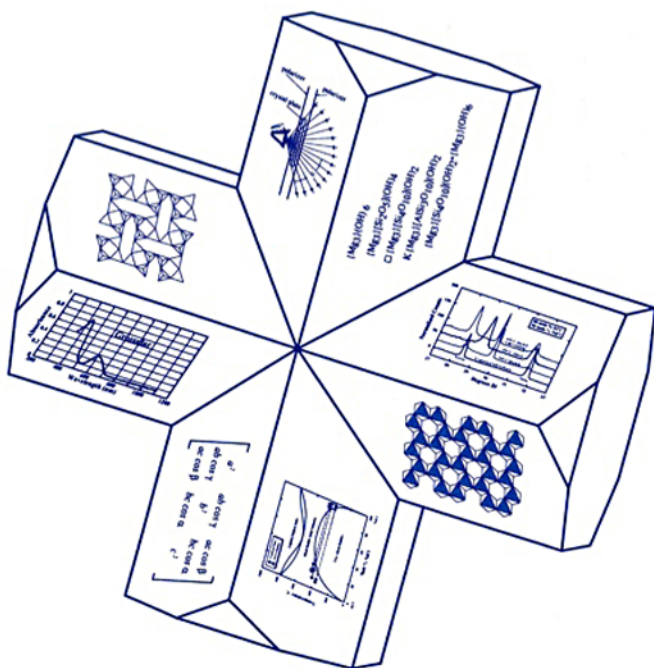


Teaching Mineralogy

Edited by
John B. Brady, David W. Mogk,
and Dexter Perkins III



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Teaching Mineralogy

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SUMMARY: A collection of exercises, activities and methods for teaching mineralogy that was assembled, classroom-tested, and reviewed by participants in an NSF-sponsored Teaching Mineralogy Workshop held at Smith College in June 1996.

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INTRODUCTION

This book is an outgrowth of a workshop on teaching mineralogy held at Smith College in June 1996 and sponsored by a grant from the Division of Undergraduate Education, National Science Foundation (DUE-9554635). Seventy participants, from diverse institutional settings and from all academic ranks, met to explore common interests in improving instruction in mineralogy. At the workshop, participants took part as both instructors and as students. They had the opportunity to explore a variety of new instructional methods and materials and also to observe their colleagues as instructors. All were encouraged to test these activities in their own classrooms, to evaluate their effectiveness, to suggest changes to the authors, and to develop new and complementary exercises. The sourcebook before you is the product of this group effort.

Teaching mineralogy is both challenging and rewarding. Mineralogy is typically taught as the first pre-professional course in an undergraduate geology curriculum. The large amount of information and abstract nature of much of the content presents formidable barriers to learning for many students. In recent years, educational scholars have discovered a great deal about the ways in which students learn. Indeed, much of the discussion at the workshop was on student learning rather than on faculty teaching. Many felt we need to be more concerned about what students can do as scientists rather than just evaluating their performance on exams.

Mineralogy, like all sciences, is a changing and expanding field. As our knowledge base continues to grow, it is appropriate to reexamine regularly what we teach and how we teach in mineralogy courses. Exciting new advances in mineralogical research, stronger connections to cognate disciplines (e.g. geochemistry, geophysics, materials science), and increasing relevance of mineralogy to society (e.g. environmental geology, resource utilization) all must be effectively incorporated into modern mineralogy courses. Our search has led us to believe that there is a convergence of the way we conduct our science and the way we teach it—and the common theme is discovery-based exercises.

There is a national mandate to reform all science education (e.g. *Shaping the Future, New Expectations for Undergraduate Education in Science, Mathematics, Engineering, and Technology*; NSF 96-139) and many in the mineralogical community are responding. New goals for science education identified in *Shaping the Future* call for coursework that is more meaningful and relevant for students in their professional training; opportunities for students to “be” scientific by simulating, replicating, or engaging true research activities; and for providing students with life-long learning skills for creative problem-solving, quantitative reasoning, clear writing and speaking, and information and data gathering. To achieve these goals, while teaching the underlying principles and knowledge base of mineralogy, is the challenge we face. New teaching approaches that may help include collaborative learning, peer instruction, alternative assessments, and especially, use of discovery- and inquiry-based exercises. We can emphasize the relevance of our course material by showing connections with sub-disciplines in geology, cognate disciplines, and society in general.

Within this volume you will find numerous exercises that can be applied in the teaching of mineralogy and related courses. There are hands-on, experimental, theoretical, and analytical exercises. All have been written with the hope of optimizing student learning. At the workshop there was little interest in developing a “prescriptive” approach to mineralogy by making recommendations on a specific content that might be universally applied in mineralogy courses and curricula. We recognize that every student population will have different needs, every faculty

member will have her or his own areas expertise, every department will have its own curricular needs, every institution will have its own resources, and every geographic setting will provide unique educational opportunities. The exercises in this volume provide examples of innovative ways that mineralogy can be taught using a variety of materials and teaching techniques. We encourage you to use these activities in whatever ways will best serve your students. You may freely photocopy the exercises for class use, adopt these materials or adapt them to meet the special needs of your own course, and use these activities as models to help you develop your own new exercises.

However you use this book, please share your experiences with your colleagues and with the authors of the exercises. Being an effective teacher is not easy and we can all benefit from the experiences of others. If you would like to join an electronic mail list server discussion of mineralogy teaching, send a subscription request to jbrady@science.smith.edu.

We hope that the exercises in this volume will help you find ways to make your mineralogy teaching more successful. If we prompt you to modify your classes so that your students not only learn and retain more, but also have fun in the process, we will have achieved our goals.

John Brady, Dave Mogk, Dexter Perkins
June 1997

DISCLAIMER

Any opinions, findings, conclusions, or recommendations expressed in this material are those of the authors and do not necessarily reflect those of the National Science Foundation.

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USING COOPERATIVE LEARNING TO TEACH MINERALOGY (AND OTHER COURSES, TOO!)

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INTRODUCTION

This chapter is concerned primarily with how the content of a mineralogy course can be organized so that the students are more active and conscientious learners. It is fairly common for students to work in groups in mineralogy labs, if only to maximize available resources. Effective lessons that help students go beyond just "working in a group" can be designed with careful application of a conceptual model of cooperative learning (Johnson et al., 1993), and many strategies, or structures (Kagan, 1992), that are simply ways to organize groups efficiently. This chapter is divided into three sections: Section I briefly describes the fundamentals of cooperative learning: why it's important and what is essential. Section II describes a variety of cooperative learning structures and their uses. Section III provides more detailed descriptions of cooperative learning activities specifically for a mineralogy class.

SECTION I: AN OVERVIEW OF COOPERATIVE LEARNING

What the research says about active learning and cooperative learning

Astin (1991, 1993) investigated 88 environmental factors to determine what influenced the academic achievement, personal development, and overall satisfaction of college undergraduates at 159 baccalaureate-granting institutions. He found that, in general education courses, the content and structure of the curriculum were far less important than the quality of interaction among students and between faculty and students -- that *how students approach* their courses and *how faculty deliver* the curriculum are more important than the curriculum itself. The findings support research indicating that a crucial factor in education is the degree to which the student is actively engaged in the educational experience. Astin's results suggest that efforts in curriculum reform might place emphasis on pedagogy and on the interpersonal and institutional context in which learning occurs.

Reflecting in the *Harvard Assessment Seminars: Second Report*, on a multi-year study of "what works" in undergraduate education, Light (1992) writes, "students who get the most out of college, who grow the most academically, and who are the happiest, organize their time to include interpersonal activities with faculty members, or with fellow students, built around substantive, academic work." Cooperative learning is a way for faculty to structure such positive interactions into their courses. Cuseo (1992) defines cooperative learning as a learner-centered instructional process that requires small, intentionally-selected groups of students to work interdependently on well-defined learning tasks.

Research in cooperative learning that focuses specifically on classroom climate and interaction (Johnson et al., 1991b) indicates that positive peer relationships are essential to success in school and that isolation and alienation are predictors of failure. When students drop out of college, they often report failure to establish a social network and failure to become involved in

their classes. Structuring academic course work to encourage cooperative interaction helps students build a sense of community that centers around their academic lives.

Research in cooperative learning that focuses specifically on achievement indicates that positive peer relationships also help students learn. Carefully designed cooperative interaction can be used to help students to: (a) share their knowledge and cultural perspectives with others; (b) articulate what they are learning in ways that help them to reconceptualize and extend their thinking; and (c) dig past the superficial. Cooperative learning results in improved critical thinking when compared to traditional lecture (McKeachie et al., 1986), and is well suited to solving complex, open-ended problems (Qin et al., 1995).

Cooperative interaction in university classrooms can help students learn essential “real life” skills. The world of work increasingly demands that individuals know how to coordinate their efforts with others on the job, know how to build trust and consensus, be good at perspective-taking and problem-solving, and be able to take initiative (Kelley and Caplan, 1993; Krackhardt and Hanson, 1993).

Mineralogy courses afford some of the best opportunities in the geology curriculum for students to work together cooperatively to solve substantive, rigorous problems. Just as students can master a body of information and become more skilled scientists over the semester, so they can also become more skilled at relating to people and working together through practice.

Promoting cooperation: a conceptual key to successful group learning experiences

Everyone who has used groups during instruction knows that merely placing students into groups and telling them to work together does not insure high-level learning or high-quality peer interactions. There are “barriers to cooperation” (Johnson and Johnson, 1994) that include:

- ◆ a lack of group maturity -- groups need time and experience to develop into high-functioning groups;
- ◆ going with the first, and often dominant, response -- groups need time and encouragement to generate many possible answers and solutions that include the efforts of all members and they need to learn how to recognize and choose which ideas to pursue;
- ◆ goofing off -- groups need to help all members learn to work hard so that everyone contributes and no one feels like a sucker;
- ◆ a fear of disagreement or conflict -- groups need to learn to manage differences of opinion and use differences to build better understanding; and
- ◆ a lack of ability or motivation to attend to both task and maintenance aspects of groups work -- groups must learn how to get the job done while simultaneously maintaining and building their interpersonal relationships.

Groups need time and practice to overcome each of the barriers identified above. **It is critically important that cooperative learning groups be used repeatedly throughout a course;** that’s why this chapter does not just describe the “cooperative learning lab.” As you will see, that does not mean you have to completely change your entire course. Small opportunities for students to interact constructively in class on a weekly basis (or more often) can make a big difference. When there is a careful application of a conceptual model of cooperative learning to specific course content, using a well-chosen structure to organize group work, students are less likely to be hampered by the barriers to cooperation and are more likely to:

- ◆ become actively engaged in learning;
- ◆ understand the material at a deeper level;
- ◆ practice and improve their skills in oral communication, problem solving, and collaborative inquiry; skills that are essential to the conduct of science.

Essential elements of cooperative learning

The conceptual model of cooperative learning includes five basic elements (adapted from Johnson et al., 1993): positive interdependence, simultaneous interaction, individual responsibility, interpersonal and small-group learning skills, and reflection and planning.

Positive Interdependence. When positive interdependence is clearly structured and understood, group members perceive that they and their work are linked for mutual benefit, that the efforts of each group member will be unique, and that the unique efforts of all members will help to maximize success. Among the ways that group members can be helped to understand that they are interdependent are through goal, resource, or role interdependence. A group sharing a set of mutual goals is fundamental to cooperative learning. The instructor clearly delineates the goals, which may be a product, a better level of understanding, or the achievement of some criteria on an assessment. Sharing resources such as materials or information is a common occurrence in mineralogy labs and can be used to promote interdependence. Role interdependence means having students in a group fulfill a set of complementary and interconnected roles in order to complete their tasks and maintain good working relationships within the group. Role interdependence can be effective at helping to equalize participation and reduce problems of differential status among group members.

Simultaneous Interaction. Students promote each other's learning by: (a) helping, sharing, and encouraging efforts to learn; (b) building both personal and academic support systems for themselves and each other; and (c) establishing norms of hard work and success. In order to promote successful simultaneous interaction, instructors need to be quite proactive when groups are formed. In general, it is best to keep groups small -- pairs for sharing, triads for diversity and a variety of ideas, foursomes to challenge the collaborative skills of group members and add complexity. Groups larger than four tend to be time-consuming and often leave some members feeling left out. It is generally best when instructors assign membership. Heterogeneity is key when assigning students to groups; not just heterogeneity by ability, but heterogeneity by gender, social status, ethnic or economic background, learning styles, collaborative skills, content preferences, and the like. In many cases, random assignment of students to groups may work well, particularly for base groups and informal groups. Students may clamor to select their own groups, but self-selected groups inevitably result in differential status and rejection that make it difficult, if not impossible, to achieve high-quality cooperation.

Individual Responsibility. Carefully building individual responsibility into group work helps to insure that students understand and contribute to the group's work and that students can individually apply the skills or concepts learned. It is important that group members know they cannot "hitch-hike" on the work of others. Common ways to structure individual responsibility include individual exams, individual journals or logs, and randomly calling on individual students to present their groups' answer.

Interpersonal and Small-Group Learning Skills. Groups do not function effectively if students do not have and use leadership, decision-making, trust-building, communication, and conflict-management skills. Some collaborative skills are essential for getting the task done, other skills are essential for building and maintaining working relationships. It is critically important that instructors address these skills directly and that students understand them.

Reflection and Planning. When students work together in groups, it is essential that they evaluate how well they have achieved their academic goals and plan what goals are still to be achieved. It is also important that they examine *how* they have reached these goals by working with others and how well they are building and maintaining their peer relationships. Reflection and planning is usually formulated by the instructor, who might ask students to focus on themselves, on each other, or on their group as a whole. For instance, an instructor might say,

- ◆ “On a scale of one to five, how well did you remember to consider all ideas?”
- ◆ “What one concept is more clear after your discussion than before? What concept remains unclear and needs more of your attention?”
- ◆ “Turn to the person on your left and tell them one thing they contributed today that helped you learn something new.”
- ◆ “As a group, evaluate your plan. Did you follow your plan? Was your plan useful?”
- ◆ “How might you modify your plan for the next lab session?”
- ◆ “Where in the work place might you need to use consensus building skills? Where in your life could you practice these skills?”

Sections II and III give some examples of how these essential elements of cooperative learning are woven into different types of activities or structures. While it is not necessary to use a particular structure, they are helpful in organizing effective groups and emphasizing positive interdependence. Don't be put off by some of the names of the structures, which may seem “elementary.” The underlying theory from social psychology is sophisticated, and they do work in college classrooms! The names are just mnemonic devices for some of the vast number of different ways to organize student work within groups.

Three types of cooperative learning groups

Cooperative interaction can be incorporated into courses through the use of informal, formal, and base groups. One or more types can be used together to help create rich, authentic, learning opportunities. The following provides more detailed information on each type of group.

Cooperative base groups. Base groups are long-term, four or five member, heterogeneous groups with the purpose of providing academic and social support. Students remain in the same base group for the duration of a course, so that the base group personalizes the course experiences. Base groups typically meet for a few minutes at the beginning of almost all classes, thereby smoothing the transition from outside to inside the classroom. Base groups provide encouragement and support in mastering the course content and skills, thinking critically and creatively about the course content and its applications to life experiences and vocation. Students can arrange to make up work following an absence through their base group members. In some cases, base group members may exchange phone numbers for this purpose, although this may not be appropriate for some classes or students.

Routines that are established by the instructor, and then continue without constant instructor intervention, are essential to well-functioning base groups. For instance, the base group routine might include:

- ◆ quick discussion of important events in students' lives (the students *will* discuss these things anyway; establishing a routine may bring students' attention back to class more quickly);
- ◆ a peer review session of practice problems, some peer editing, generating questions from or brief discussion of assigned reading;
- ◆ progress reports and problem solving about long-term individual assignments;
- ◆ collection and distribution of course work (a real time-saver in large classes).

One possible extension of the base group concept is their use as the foundation for out-of-class study or discussion groups. The *Harvard Assessment Seminars* (Light, 1990; 1992) found that students who form study groups report that they learn more and enjoy their academic work more. Even students who report that they prefer to work alone, benefit academically from being required to participate in a study group. Over time, study groups become a kind of social support network. Interestingly, women were found to be far less likely to join or start a study group than

men. One of two suggestions made most often by students in the study was that instructors encourage student study groups, even make them part of the course syllabus. The routine and structure of in-class base groups can provide students with a head start for the development of meaningful out-of-class meetings.

Base groups (meeting in or out of class) are not the place for high stakes academic work; i.e., work that has a direct and significant impact on students' grades. Most base groups do not have any formal or graded academic tasks. However, in some classes, base groups are given out-of-class tasks, such as an "exam" or "movie night" requiring substantive, collegial discussion structured around course readings or other assignments. In a field techniques course, students were required to complete a semester-long project in groups of about 3 students as the major portion of their grade. Having students meet and work in class in base groups with different membership provided a sounding board for students to discuss problems with their project groups, and significantly improved the functioning of most project groups. Activity 1 in Section II describes the format of a base group activity developed for an upper-level education course.

Informal Groups. Informal cooperative learning groups (Johnson et al., 1992) are short-term, heterogeneous groups. Instructors select members at random or intentionally. Informal groups are typically used during relatively long, direct-teaching episodes such as lectures or videos. Informal groups also can be used in combination with formal work groups in order to provide a change of pace, move students around the class, and promote peer discussion. The primary purposes of informal groups are to help:

- ◆ create a mood conducive to learning;
- ◆ focus student attention on the material that is to be learned;
- ◆ maintain student attention by dividing the material to be learned into shorter segments;
- ◆ create regular opportunities for oral rehearsal, semantic organization, and elaboration to help students process cognitively the material being taught;
- ◆ provide opportunities for students to identify misconceptions and gaps in knowledge within the relatively safe context of a small group;
- ◆ provide learning opportunities for all students within a group, reducing isolation and mitigating status differences in the classroom;
- ◆ promote the benefits of giving and receiving peer explanations; and
- ◆ provide closure.

Using informal cooperative learning groups with direct instruction can be as simple as asking a question and, instead of treating the question rhetorically or having students raise their hands and respond in front of the entire class, asking students to turn to the person next to them for discussion. Providing closure can be as simple as using the last 5 minutes of class to have students discuss a question that helps them summarize and synthesize the material that has been presented.

When applying cooperative learning, it is useful to consider how students will group and with whom they will talk. Most instructors can arrange the seating in their classrooms so that "turn to your partner" or "discuss in your foursome" is quite simple. However, many students have a tendency to always sit in the same spot near the same people. It may be important to ask students to move out of their seats to talk with classmates, in order to reduce feelings of isolation and to increase opportunities for community building. Several activities for informal groups in Section II are designed to move students around the classroom in interesting ways. Students are commonly resistant to moving around, but moving among groups generates more ideas and can significantly improve skills. If you regularly use structures that ask students to move around the classroom, resistance will diminish.

Sometimes it is useful to provide guidance about how students should talk, for how long, and with whom. Such guidance can mitigate some of the status differentials that exist in all classrooms. Status differentials within groups may be perceived by the instructor as immutable personality traits; in reality, however, students have different types of status in different life situations, and status is not necessarily a reflection of academic performance. In simplest terms, the student who dominates the group does not always have the right answer! Several cooperative learning structures described in Section II can help to equalize participation and learning opportunities for all students in a group; for example, by requiring students to share ideas in turn, or by preventing a student from speaking a second time until every student has spoken once.

The informal group structures in Section II are arranged roughly in order of increasing complexity and sophistication. Each example provides information about what is good about that particular structure, and what interpersonal and small-group learning skills are practiced in the structure. For example, to promote the interpersonal skill of good listening, each student can be asked to present the ideas of another member to the group. The word “informal” can be deceptive as a description. Informal groups may look and feel quite casual in the classroom, but instructors who use informal groups know that thoughtful planning can greatly enhance effectiveness. By browsing through Section II, you can get a good idea of which structures work in different kinds of classroom settings or with different kinds of content objectives.

Formal Groups. Formal cooperative learning groups (Johnson et al., 1992, 1993) are carefully structured, heterogeneous groups, in which members work together to complete specific tasks which may take a class period or several months. Membership is stable over that time. The distinction between informal and formal groups is not always sharp, but the level of complexity, both of the work content and the depth of peer interactions, is greater in formal groups. As you can see by browsing in Section II, most formal group structures involve material that is complex enough that students benefit from examining the material in pieces or from different perspectives, and then synthesizing and reconceptualizing the material. In formal learning groups, students share:

- ◆ a goal to maximize the learning of all members;
- ◆ both individual and group responsibility for their learning goals;
- ◆ specific work goals that are to be accomplished cooperatively;
- ◆ opportunities and obligations to learn and use the interpersonal and small-group skills that are needed to get the job done and build and maintain effective peer relationships; and
- ◆ opportunities and obligations to reflect on, and analyze, both learning and peer interaction.

When students need to work and stay together to get the job done, positive interdependence is key. Resource interdependence is common and may be used as a major learning device in an activity. Role interdependence is useful when a task is complicated or controversial. If formal groups are used to complete tasks that require considerable out-of-class work, or that have significant impact on the students' grades, it is critically important to devote some class time to the group work in order for all students to reap the benefits of learning cooperatively. Cooperative learning should never become just an excuse to direct students to “learn it together on your own time.”

Groups can benefit from learning about other groups' work. Typically, intergroup sharing consists of groups standing and reporting what they have done. This is time consuming and often boring. Worse yet, only one group can talk at a time, which does not provide opportunities for students to actively process and reconceptualize the work of their peers. Cooperative learning structures that provide alternatives are listed in Section II.

A conceptual model of lesson design incorporating cooperative learning

There are so many elements, so many structures, and so little time. How do you decide what and how to implement? Certain principles of learning and lesson design, well summarized by Hunter (1982), can be used to make informed decisions and maximize learning opportunities.

Anticipatory set. An anticipatory set serves as a kind of warm-up or motivator to focus the students' attention on what is to be learned. A set can be used, for example, to determine what students already know about a subject. Anticipatory sets can be incorporated into any kind of cooperative learning group at the beginning of the work in order for students to share what they know, find out what others know, and motivate everyone to work together to learn more.

Understanding the objective. It is helpful if students understand the purpose of what they will be doing or learning, and how the experience fits into the larger picture of the course. It is helpful if students understand that *how* they are being asked to learn impacts on *what* and *how much* they are learning. This can be incorporated into progress checks, typically conducted by base groups or long-term formal groups.

Input and modeling. Students need to learn basic information and skills so that they can organize, reorganize, and extend them to more complex concepts and processes. Informal learning groups can be used to keep students active and to give them opportunities to reconceptualize the material being presented during lecture or demonstration. When it seems appropriate for students to take the lead in organizing, explaining, and reconceptualizing information, formal work groups are a good choice.

Practice. Students need opportunities to practice using the information, concepts, and skills they are learning. In general, having students practice independently should follow some sort of guided practice so that both instructor and students are reasonably confident that independent practice will help students to move towards fluency rather than to reinforce mistakes. Cooperative learning groups of all types are ideal venues for students to conduct guided practice and discuss results of independent practice.

Closure. Closure, reflection, and planning are essential for high-quality learning and community building in the classroom. The purpose of closure is to help students reflect on what has been learned as well as what needs to be learned, on how it has been learned as well as how it might be learned. Students benefit from having a brief closure activity at the end of *each* class, so it is important for instructors to resist the temptation to lecture or allow a lab to continue until the last possible moment of class. The one-minute paper, developed by Charles Schwartz at the University of California at Berkeley, (Cross and Angelo, 1988), is one way to integrate closure into the instructional routine. A few minutes before the end of class, students are asked to respond to two basic types of questions: (a) What was the most important/meaningful/useful thing you learned today?; and (b) What question do you still have or what remains unclear? These questions may be discussed or answered in any type of cooperative learning group. When students have worked together in formal groups, closure generally should include some reflection on how the group has worked together, as well.

Assessment: Checking for understanding. Checking to insure that students are learning the information and/or skills needed to accomplish the course objectives may be in terms of a formal (summative) assessment, or a less formal (formative) assessment. Checking for understanding does not necessarily mean something instructors "do" to students; students can learn to check their own understanding and that of their peers. Formative assessment can be incorporated into cooperative learning designs in many ways; for example, through one-minute papers, instructor monitoring of group work, and carefully selected questions for reflection and

planning. Cooperative learning structures may be used to help a group probe the understanding of individual members, or to help students check that they understand others' ideas.

Cooperative learning can help to separate learning opportunities (or formative evaluations) from testing (or summative evaluations), and can help the instructor to more clearly define and distinguish the role of each in determining students' grades. This distinction helps instructors to develop a grading strategy that reduces students' anxiety that grades may be dependent upon less conscientious members of a group. There is not necessarily a direct connection between summative assessment and cooperative work. Individual responsibility checks, in the form of tests, papers, and the like, are quite often independent of the group work that has helped students to develop and deepen the understanding that is to be assessed. However, when it seems reasonable to combine assessment with some group product or process, there are a few principles to keep in mind:

- ◆ keep the stakes within reason -- one group project, good or poor, should not make or break a student's grade;
- ◆ connect group responsibility and assessment with individual responsibility and assessment -- facilitate this by asking groups to hand in their group work plus individual preparation and contributions in the same folder;
- ◆ ask groups to participate in the development of criteria to assess group work; and
- ◆ ask groups to develop their own contracts for group work so that each student articulates what, and how, they are expected to contribute to the group.

SECTION II. EXAMPLES OF COOPERATIVE LEARNING STRUCTURES

Base Groups

1. Base Group Exam

About three weeks before the exam due date, you will each receive a list of discussion questions. To complete the group exam, you must meet with your base group and discuss the content of your assigned readings plus other readings you have done. Find a comfortable spot for your group to meet and plan to spend about three hours together. (Sometimes base groups find it useful to divide this meeting into two sessions). The purpose of the group exam is to have a thorough, intellectually stimulating, creative, fun, and practically useful discussion. More specifically, the task is to demonstrate deeper understanding of the assigned reading. In addition, the group discussion should provide an opportunity to generate ways to apply the concepts we focus on in class.

Remember: This task is to be accomplished cooperatively.

The responsibilities of each base-group member are as follows:

- ✓ Choose two questions to prepare for the discussion. (Make sure these questions are different than the ones others are preparing.)
- ✓ Prepare answers and discussion items based on your readings, course experiences, and other resources. You will be the group expert for your questions.
- ✓ Prepare for the group discussion by developing handouts, visuals, or anything else that you think will help your group understand the material--use good teaching techniques!
- ✓ Come to the exam prepared to contribute to the discussion and to think critically and creatively. Bring to the discussion (a) a typed synopsis of your response to each question with relevant page numbers in assigned readings, (b) copies of relevant written information to facilitate discussion, and (c) supplemental materials.

When your group meets for the exam, cover at least one question from each member. Since each member has come prepared to discuss two questions, your group should be able to engage in rich discussion.

While at the group meeting your job is to:

- ✓ Stick to the question.
- ✓ Be conscious of the time.
- ✓ Be specific, positive, and descriptive.
- ✓ Encourage constructive disagreement.
- ✓ Take responsibility for both the task and maintenance actions in the group. (Your group has a task to accomplish and the discussion should also be enjoyable and satisfying.)

To document that the group discussion exam has taken place, and that the criteria for passing has been met by all group members, each member will be required to sign a certification form. Make sure that there are no free-loaders. Do not sign off for a group member unless s/he arrived for the exam fully prepared and participated actively in the discussion of each question.

Group grade: Each group will be expected to submit a summary report consisting of:

- ✓ the certification form;
- ✓ a list of the questions discussed with a summary of answers and conclusions generated;
- ✓ a description of the procedures followed; and
- ✓ a subjective evaluation of the learning resulting from the experience. Each group member should be an integral part of this summary writing and should proof-read all the work.

Individual accountability: On the day the project is due, individual group members will hand in copies of the materials they prepared of the discussion.

Informal group structures

What's good about these structures: They are simple to use. Students have an opportunity to think by themselves. All students have an opportunity to share their ideas and hear the ideas of others. In the Three-Step Interview, students also hear their ideas explained by a peer, explain the ideas of a peer, and hear the ideas of three peers.

Interpersonal and small-group skills: Sharing an idea, careful listening, asking clarifying and probing questions, and paraphrasing.

2. Think Pair Share (Lyman, 1992)

Group size: two

1. Instructor asks a question or poses a problem. Students think by themselves.
2. Students pair and discuss their ideas.
3. Individual students are called upon to share their answers (or the answers of their partners) with the whole class.

3. Think Pair Square

Group size: two and four

1. Instructor asks a question or poses a problem. Students think by themselves.
2. Students pair and discuss their ideas.
3. Each pair teams up with another pair and shares in their foursomes--a square.

4. Three-Step Interview (Kagan, 1992)

Group size: two and four

1. Instructor asks a question or poses a problem. Students think by themselves.
2. Students pair. Within pairs, students each spend a moment or two sharing their ideas and being interviewed by their partners.
3. Each pair teams up with another pair and creates a foursome. Within foursomes, students each share their partner's ideas with the other pair.

Informal group structures that mitigate issues of status and motivation

What's good about these structures: They are fairly simple to use. Students think by themselves. All students, regardless of status, have opportunities to share their own or their group's ideas and to hear the ideas of others. Accountability is enhanced because all students are equally likely to be asked to report, or ideas are written down before discussion, or students are obligated to share the group's ideas with other groups. Sharing can be equalized to lessen status problems by asking students to share one at a time. These structures can help instructors avoid typical questioning patterns that may be related to perceptions of ability or issues of race or gender. It helps students move past perceptions of "She always calls on him," or "He only calls on me when he thinks I don't know the answer."

Interpersonal and small-group skills: Sharing an idea, taking turns, careful listening, asking clarifying and probing questions, paraphrasing, moving in an organized way, or being responsible for the group's work.

Informal group structures that mitigate issues of status and motivation, continued

5. Numbered Heads Together (Kagan, 1992)

Group size: Three or four

1. Students count off in their groups.
2. Instructor asks a question or poses a problem. Students think by themselves.
3. In groups of three or four, students discuss their ideas.
4. Instructor uses numbers to randomly call on students to report on group discussions.

6. Group Interview

Group size: three or four

1. Instructor asks a question or poses a problem. Students think by themselves.
2. Each student is “interviewed” for a minute or two by the other members of the group.

7. Pens in the Middle

Group size: three or four

1. Instructor asks a question or poses a problem. Students think by themselves.
2. In groups of three or four, students share their responses. When students share, they each place a pen or pencil in the center of the group to mark a contribution. Students can not share a second idea until all pens are in the middle.
3. An instructor might monitor the group by picking up a pen, asking whose idea the pen represents, and asking that person or a different group member to describe the idea.

8. Roundrobin (Kagan, 1992)

Group size: three or four

1. Instructor asks a question or poses a problem. Students think by themselves.
2. In groups of three or four, students “go around” and, in turn, share their responses.
3. Sometimes instructors find it useful to have students count off. They can then help organize the sharing by saying, “Start with person # 3 and share clockwise.”
4. Instructor may use numbers to randomly call on students to report on group discussions.

9. Roundtable with Roundrobin

Group size: three or four

1. Instructor asks a question or poses a problem. Students think and write by themselves. Writing responses before sharing helps when groups have status problems, when one or more members are not motivated, or when students find it hard to express their own ideas.
2. In groups of three or four, students “go around the table” and, in turn, share responses.
3. Sometimes instructors find it useful to have students count off. They can then help organize the sharing by saying, “Start with person # 3 and share clockwise.”
4. Instructor may use numbers to randomly call on students to report on group discussions.

Informal group structures that mitigate issues of status and motivation, continued

10. Stirring Up the Class

Group size: three or four

1. Students count off in their groups.
2. Instructor asks a question or poses a problem. Students think by themselves.
3. In groups of three or four, students discuss their ideas.
4. All students # 1 rotate one group and share their old group's discussion and answers with the new group.
5. Instructor asks a question or poses a problem. Students think by themselves.
6. Students discuss their ideas.
7. Rotation procedure is repeated. This time, students # 2 rotate two groups and share their old group's discussion and answers with the new group.

Informal group structures particularly useful for review and closure

What's good about these structures: These structures work well for review and closure. Students have an opportunity to move around the room and share with several peers. All students have an opportunity to share their ideas, see how their ideas relate to the ideas of others, and give and receive feedback.

Interpersonal and Small-Group Skills: Sharing ideas, careful listening, asking clarifying and probing questions, offering or asking for help or information, adding to the ideas of others, giving and receiving feedback, paraphrasing, synthesizing or summarizing information, moving in an organized way.

11. Mix-Freeze-Pair (Kagan, 1992)

1. Students mill, or mix, around the room. When the instructor says freeze, students stop.
2. When the instructor says pair, students form pairs--turning to the person closest to them.
3. Instructor asks question.
4. Students discuss question.
5. Process is repeated several times so that students have an opportunity to talk with several peers. When there is an odd number of students in the class, each grouping will result in one trio. Part of the routine might be: Ask the trio to raise their hands and then announce, "The next time we pair, make sure that these three classmates are all in pairs--not in a trio."

12. Find Someone Who Knows or Treasure Hunt

1. Instructor creates a worksheet related to academic content (Find Someone Who Knows) or to personal information (Treasure Hunt).
2. Students mill around the room and gather information from their peers. Students may be asked to sign a worksheet when they provide a piece of needed academic information.
3. Students share information they have gathered. This can be done as a whole class, in base groups or work groups; it can be written or entered by computer on some type of chart or graph.

Informal group structures particularly useful for review and closure

13. Rotating Review (Kagan, 1992)

Group size: three or four

1. Instructors asks a series of questions or presents several topics. These are posted around the classroom--on large pieces of paper or on blackboards.
2. Each group of students is assigned to one topic or question. They move to that area, discuss the idea for a moment, and write a response.
3. The instructor signals. All groups move to the next question or topic, read what has been written, write comments or questions, and add something new. This continues until the groups return to their first positions. (It is helpful if each group uses a different color chalk or marker.)

14. Inside-Outside Circle or Mad Hatter's Tea Party

1. Students form two circles--the inside circle faces out and the outside circle faces in. (If the classroom lacks floor space, two smaller concentric circles will work.) In Mad Hatter's Tea Party, students face each other in two lines.
2. Instructor asks question or presents a discussion topic.
3. Students talk with their partners. This can be done freely or can be directed by the instructor. For instance: "People in the outside circle, you have one minute to explain your position. If you are in the inside, you may ask questions but not share your own ideas."
4. Students move to new partners--it is easier for the outer circle to rotate. In Mad Hatter's Tea Party, either one line shifts or both lines shift but in opposite directions.
5. When students move to a new partner, they might first paraphrase what their old partner said before beginning a new discussion.
6. Pairs are determined by the movement of the circles or lines. This may be preferable when there are inclusion or status difficulties in a classroom or when free movement may be too chaotic.

Informal group structures particularly useful for making comparisons or discussing controversies

What's good about these structures: These structures emphasize exploring ideas thoroughly, comparing and contrasting ideas, and making careful distinctions among differing opinions. Students have opportunities to move around the room, think by themselves, declare their ideas and preferences publicly, and learn about the ideas and preferences of others.

Interpersonal and Small-Group Skills: Sharing ideas, stating your opinion, careful listening, asking clarifying and probing questions, offering or asking for information, adding to the ideas of others, giving and receiving feedback, paraphrasing, making distinctions, synthesizing or summarizing information, moving in an organized way.

Informal group structures particularly useful for making comparisons or discussing controversies, continued

15. Corners (Kagan, 1992)

1. Instructor announces the corners. Corners are often related to student preferences or choices: "For the lab, would you rather make observations about the effects of water, sunlight, temperature, or soil acidity on plant growth?" You might ask students to make comparisons or applications: "The most important metal today is gold, iron, copper, or aluminum?" You might ask students to think in analogies and metaphors: "Is research on the Internet--'A Highway To Heaven,' 'Easy Street,' 'A Long And Winding Road,' or 'A Road Less Traveled'?"
2. Students each think (and perhaps write) by themselves.
3. Students move to their preferred corners.
4. Students discuss their reasons with others in their same corner. (Three-step Interviews or Group Interviews might be used if students have a difficult time sharing or listening.)
5. Students are called on to paraphrase the different ideas they have heard in their corners. (Students who went to the same corner may have different reasons for doing so.)
6. Students might be asked to paraphrase--verbally or in writing--reasons for all four corners.
7. Corners might be used to form work groups: Students from the same corner--students with similar interests or preferences--could work together; students from different corners--students with different interests or preferences--could work together.

16. Value Lines

1. Instructor announces a statement or question with two poles and implied "shades of gray" in between. Like corners, these statements help students discuss preferences and choices, make comparisons and applications, or encourage metaphorical thinking. For mineralogy, using Value Lines to explore the asbestos controversy is an obvious choice.
2. Students think by themselves.
3. Students position themselves on an imaginary line--asking questions and explaining their positions so that they know where to stand.
4. Once students are in line, they might talk with those near them to hear why others have chosen similar views. The line might also be "folded in half" so that students with extreme positions have an opportunity to hear views that are different from their own.

Formal group structures

What's good about these structures: All students, regardless of status, have an opportunity to share their information and gather information of others. Students have an opportunity to practice many cognitive skills--including sequencing, descriptive language, deciding what is important, looking for details, comparing, contrasting, and synthesizing. Students have opportunities to conceptualize, reconceptualize, and teach information or procedures to others.

Interpersonal and Small-Group Skills: Sharing information (and knowing when and what information is needed), careful listening, taking turns, asking clarifying and probing questions, offering or asking for information, adding to the ideas of others, giving and receiving feedback, paraphrasing, making distinctions, organizing, synthesizing or summarizing information, teaching.

17. Jigsaw (Aronson et al., 1978)

Group size: three or four

1. Instructor divides material into sections--one section for each student. Students are assigned to groups (call these Groups 1).
2. Students prepare their own section of material--they read, conduct an experiment, solve a problem, etc. This preparation might be done alone--in class or for homework--or with a "preparation partner," depending on the nature of the assignment and abilities of the students.
3. Students each meet with one or more people from a different group who has/have learned the same material. The purpose of this group is both to review and reconceptualize the material and to plan how the material might be best taught or presented to teammates in Group 1.
4. Students move into their "Groups 1" and present their work to the other members. Instructors encourage students to ask questions and engage in genuine discussion--not just passive listening.
5. A summary or synthesis product results from the group work to provide closure for the task.
6. Students process the presentations and the information they have learned. Sentences such as "You helped me learn this material when you . . ." and "One new idea I learned today was . . ." are useful prompts for processing.
7. Individual mastery of students is assessed.

Formal group structures, continued

18. Blind Hand

Group size: three or four

1. Instructor divides material and each student receives one (or two) piece(s) of material.
2. Students each examine their own piece of material to make sure they can describe the details.
3. Students work together to determine the sequence or to describe the entire event that they each "have a piece of." The rules of Blind Hand are:
 - a. You can tell (or read) what is on your paper, but you can't show it.
 - b. You can ask questions.
 - c. You can take notes and share your notes.
4. Once students think they have determined the sequence or solved the problem, they put their resources together, in sequence, and look at "the whole picture." Before they check their work, it is often useful to ask students to reflect, as individuals, about how confident they are that their group's work is "accurate" or "makes sense."
5. Students process their work together. Planning how to proceed is often an essential skill with Blind Hand and it may be useful for students to discuss "Did we have a plan?" "Did our plan work?" "How did we decide what was important?"

Formal group structures that involve investigations of controversies or projects

What's good about these structures: Students have many opportunities to think for themselves, to make choices, to share information and experiences with others, to participate in collective inquiry, to develop well-reasoned arguments, and to practice the skills of idea differentiation, perspective taking, and consensus building. The research on the Academic Controversy structure suggests that students develop both greater understanding of the subject matter and good skills for managing controversy constructively (Johnson and Johnson, 1992). A topic such as the environmental hazards of mineral dusts or the costs and benefits of resource extraction might be particularly appropriate for Academic Controversy. The steps of a Group Investigation, when well planned and facilitated by a skilled instructor, help students to have both the opportunity and the responsibility to contribute to the classroom learning community.

Interpersonal and Small-Group Skills: Many skills are used in these complex, long-term structures, including making choices, planning, asking questions, integrating ideas, taking perspective, building reasoned arguments, disagreeing in an agreeable way, extending the ideas of others, and integrating different ideas into coherent positions.

Formal group structures that involve investigations of controversies or projects, continued

19. Academic Controversy (Johnson and Johnson, 1992)

Group size: four

1. Instructor prepares statements to be discussed.
2. Students are assigned to groups of four. Within each foursome, students are assigned a partner and a position. Students work with partners to prepare reasoning for positions.
3. Each student meets in a "preparation pair" with a student from another group who has prepared the same position. The purpose is to reconceptualize and share materials and strategies.
4. Students meet again in their original pairs, compare notes and finish preparing positions. "Our best case is. . . ."
5. Each pair of students presents their position to the original foursome while the other pair listens and takes notes. "The answer is . . . because. . . ."
6. The two pairs enter into an open discussion. "Your idea is wrong because. . . . My idea is right because. . . ."
7. The two pairs reverse perspectives. Each pair now prepares a new argument.
8. The two pairs present their new arguments and points of view. "Our position now is . . . because. . . ."
9. The two pairs drop advocacy and work together to build a well-reasoned synthesis. "Given what we now know, our best reasoned judgment is. . . ."

20. Group Investigation (Sharan and Sharan, 1992, 1994)

Background: The instructor begins by choosing a problem that is worth investigating and can be investigated in a variety of ways. The instructor collects information. This helps the instructor to determine if the overall problem is "doable" and helps the instructor to "get organized." These materials help to motivate students and provide students with a "starter kit" of resources. The instructor presents the general problem, question, or topic that is to be investigated.

1. The class scans their resources, discusses their interests and priorities, determines subtopics, and organizes into research groups.
2. The groups plan their investigations. They further refine their questions, divide their work, and assign roles to help them manage their work as a group.
3. The groups carry out their investigations. The instructor is an active facilitator--helping groups plan, organize, and pace their work and helping them develop and use the skills they need to build and maintain their interpersonal relationships.
4. The groups plan their presentations. During this phase, the groups must decide what they have learned in their investigations and how to organize and present their findings. Presentations need to be interesting and need to include each group member. Sometimes representatives from each group form a steering committee to schedule the presentations of different groups.
5. The groups make their presentations.
6. The groups evaluate their work--as individuals, as groups, and as a class.

Presenting results in interesting ways

What's good about these structures: All students, regardless of status, have an opportunity and responsibility to share and gather information, and to practice giving and receiving feedback about work. Students have an opportunity to practice many cognitive skills, including the use of descriptive language, deciding what is important, looking for details, comparing, contrasting, and synthesizing. Everyone gets to talk at once in an organized manner.

Interpersonal and Small-Group Skills: Sharing and comparing ideas, asking questions, moving in an organized way, giving descriptive, positive feedback.

21. Gallery Tour (Kagan, 1992)

Group size: three or four

1. Students have worked together, in their small groups, to solve a problem, complete an experiment, or create a visual such as a story map, chart, graph, etc. This structure is best used when groups have produced a tangible product.
2. These products are hung or otherwise displayed around the room.
3. Students rotate, with their work groups, around the room to visit and discuss each display. (This is best done in an organized way with some signal from the instructor to indicate when it is time for students to move.) Typically students take notes or each group leaves a piece of descriptive feedback at each display. This can be done by using post-its or by using feedback forms that have been specifically designed for the particular activity.
4. Students return to their own work. They might discuss the feedback that has been left by other groups; they might discuss how their work was the same or different than other work they saw; they might add an idea to their work that they gleaned from the work in another group.
5. Students process their work together.

22. One-Stay Three-Stray

Group size: three or four

1. As with the Gallery Tour, this structure is used when group products are displayed.
2. Students count off in their groups.
3. The #1 person in the group rotates one group, the #2 person rotates two groups, and, in a group of four, the #3 person rotates three groups. (Each one of these steps is best done one-at-a-time to eliminate confusion.) One person stays "home." Students are now in totally new groups.
4. The person who "stayed home" now explains their old group's work to the visitors. The visitors frequently take notes and often ask questions to make sure they understand. The visitors give one piece of specific positive feedback to the home group representative about that group's work. They thank the representative for staying home to explain the group's work.
5. Everyone moves back to their home team. First, the person who stayed home tells the other group members what positive things the visitors have said about their work. Next, persons #1, #2, and #3 explain what they have seen in different groups--comparing and contrasting the ideas and formats to their own.
6. Students process their work together.

SECTION III: EXAMPLES USING COOPERATIVE LEARNING IN MINERALOGY

Using informal groups on the first day to begin creating the cooperative classroom

The first day of class can be used to advantage to set the tone for the entire course. Usually mineralogy is an upper-level course for majors, but students may not be ready to begin complex material on the first day. At West Chester, sophomore-level "Minerals and Rocks" is one of the first courses majors take. It is beneficial to use the first class period for the students to get to know one another, for the instructor to gather useful information about the students, and to begin establishing a climate of cooperation.

1. The first activity in the class is used for students to get to know one another and to make the transition from outside to inside the classroom. For example, the instructor may use the Three-Step Interview structure. After roll is called, students are divided into groups of two. For example, in a class of 17, students count off from one to eight, then find the other person(s) with the same number to create seven groups of two (numbers 2-8) and one group of three (number 1). Other methods can be used to put students into groups at random; for example, by handing out index cards with numbers or colored dots ("find someone with the same/different color"); or even by having students select one of a group of minerals ("find the other person with the same/different mineral"). Groups are then directed to "take five minutes to interview each other and find out: your partner's name (first and last); what degree program or major s/he is in; and ONE thing your partner did this summer or over winter break." The instructor tells the groups to make sure everyone has a chance to speak, and that each student will introduce the other to a new group in the next step. This requires students to listen carefully as well as talk. After five minutes, the instructor then directs each pair (or threesome) to join up with another pair, either by proximity, by numbers (e.g., odd numbers together), or by some other method. The new groups (of four or five members) are given five minutes for each student to introduce his/her partner to the new people, thus completing the Three-Step Interview.

2. Additional group activities can be used to collect information that will be useful to the students and to the instructor. For example, the instructor may want to know when and where each student took introductory chemistry, and if anyone has taken a more advanced chemistry course. The instructor may wish to assign students to heterogeneous base groups (or work groups) based on the number of credits completed or specific interest in geology. In order to facilitate the formation of out-of-class study groups, the instructor may want to group students based on other courses they are taking (e.g., calculus or historical geology). This type of information is easily and quickly collected on the first day by giving each group of four or five students one large index card and asking one person in each group to record the information. Having the instructor designate the recorder prevents the common occurrence of groups automatically designating a female member to be the recorder. The instructor can equalize sharing and listening by directing the students to speak in turn beginning with the recorder. A student other than the recorder can be designated to introduce the group members to the class, in order to increase participation by all group members and to connect groups with the rest of the class. This typically takes 1-2 minutes per group for a brief introduction (in the example above with 17 total students, this would take about 4-8 minutes).

3. The instructor may use the groups for more complex tasks, such as reviewing important information on the syllabus or reviewing material from previous courses. For example, each group may be directed to focus on one small part of the syllabus, take five minutes to discuss and summarize the information, and then report to the class. Using this format, students pay more attention than when the instructor reads the syllabus to them. Having students articulate what they remember about course content from previous experiences is one of the most productive ways to use the first week of class. In the Minerals and Rocks course, for example, groups would be given a large sheet of easel paper and some colorful markers and asked to write down everything

they remember about a topic in the course, such as igneous rocks. The instructor can remind the students that they are not expected to have perfect memories, and ask them to flag information they are unsure of and write down any questions they have. These papers can then be used by the instructor as a springboard to provide an overview of the course. The papers can be brought out later in the course and used to introduce new topics, to build understanding, and to identify and correct misconceptions. Such complex work is probably not appropriate for the very first day of class, unless the class meets for several hours once a week.

4. Closure on the first day can be very simple: "Thank your partners for working with you today." More extensive closure activities, such as reflecting on the day's work, can be used if more complex tasks were accomplished.

Using informal groups during lecture

This example describes the simplest way to incorporate cooperative learning into an otherwise traditional class. Asking students to talk with each other about course content has the potential to increase preparation for and participation in class. The key is to use the structures frequently, once a week or more often, particularly during the first few weeks of class in order to establish norms. If students don't come prepared to discuss reading, this structure lets them know that that behavior is unacceptable.

1. The lecture will cover fairly technical content including previously-assigned reading. Instructor puts students in groups of three or four and students count off within groups. Instructor gives students two minutes to think about the questions: "What is one concept you think you understand from your reading?" "What is one thing you need help to clarify?" Instructor gives students five minutes to share their responses in groups, talking in turn starting with "person #2;" students are reminded that each member of their group needs to share responses to both questions within five minutes, (Roundrobin structure). While they talk, instructor walks around and listens to get a sense of how to focus the lecture.

2. Lecture begins; instructor stops about one-third to half-way through time period and puts on an overhead to present students with a problem that is related to the concept they are learning. Students think -- by themselves -- about how they might solve the problem using the information they are learning. Then students take three minutes to share their ideas with their groups and decide on at least one possible way they might solve the problem. After three minutes, instructor calls on one or more students by number and group at random to share their group's idea, (Numbered Heads Together structure). Lecture continues, incorporating additional problems or concept questions, as appropriate.

3. As an alternative to step 2 above, instructor may stop after about ten minutes and put on an overhead to present students with a problem that is related to the concept they are learning. Students think -- by themselves -- about how they might solve the problem using the information they are learning. Then students take three minutes to share their ideas with their groups and decide on at least one possible way they might solve the problem. After three minutes, instructor asks all "persons #1" to stand, rotate one group around the room, and share their group's ideas with a new group, (Stirring Up the Class structure). This process is repeated as lecture continues. The second time, "persons #2" are asked to rotate two groups; the third time "persons #3" are asked to rotate three groups; the fourth time, "persons #4" are asked to rotate.

4. For closure, instructor gives students five minutes to reflect and discuss the questions: "What is one concept that today's class helped you to clarify?" and "What concepts are still fuzzy?" Instructor asks the group to summarize responses in writing and turn in. Alternatively, instructor may ask students to write down what they think is the most important concept of the day, and have groups collect, discuss, and turn these in. Instructor uses the responses to aid in planning.

Using cooperative learning groups and worksheets as an alternative to lecturing: an example for teaching close-packed structures and coordination

The instructor is using two 90-minute lecture periods to present material on close-packed structures, cation sites, coordination, and Pauling's Rules. Lecture is kept to a minimum at the beginning and end of the periods. Instead, the instructor has created two worksheets for the students to complete during class time in order to help them to actively discover, or construct, their understanding of the concepts by playing with models of crystal structures. The cooperative learning groups are long-term (two class periods) but the interactions among group members are quite unstructured. If status or motivation issues are a problem, participation could be equalized by assigning roles to students in the groups, or by assigning specific questions on the worksheet to individual students. The instructor also could simply monitor the groups by calling on group members at random frequently during the class periods.

1. In the first 90-minute lecture period, the instructor divides the class into groups of 2-3 students. Each group is given a tray containing 20-30 styrofoam balls, all of the same size, and a worksheet with a set of instructions and questions. Over the class period, the groups arrange the balls to exhibit different types of close packing, visualize how smaller atoms could fit in the spaces between the layers of styrofoam balls, and answer questions about the atomic arrangements and concepts involving coordination number. The students have to work together, not only to complete the task and share resources, but also to hold the balls in place and keep them from rolling around the box! This subtle but effective lesson in cooperation is lost if groups are larger than 3 students.
2. During the last few minutes of the period, the instructor asks one person from each group to summarize a key piece of information, such as, "How does the size of a site change with coordination number and why?" The instructor asks each person in the class to write down any concepts that are still not clear, and gives the reading assignment from the text that covers the same material as the worksheet and anticipates the next period's material.
3. During the second 90-minute lecture period, the instructor has the students move into the same groups and discuss any questions they still have about the material. After about 5 minutes, students write the most important remaining question on a big sheet of paper or on the board. The instructor introduces the day's topic and objectives (the anticipatory set), in the process answering some questions immediately while highlighting others as topics to be clarified during the day's activity.
4. The instructor then gives each group a worksheet of questions. The groups circulate around the room examining models of different crystal structures. Each group is responsible for answering all questions on their worksheet. Another copy of the worksheet has been left at each model, and each group is also responsible for answering a subset of the questions on these worksheets. When a group arrives at a particular model, they answer all questions on their worksheet and fill in the answers to their subset of questions on the worksheet next to the model. The next group who visits that model answers a different subset of questions on the worksheet next to the model. In answering the remaining questions on their own worksheet, they may compare their answers to those of the previous group. If they disagree with any of the answers of the other group, they can put a sticker or a ? next to those answers. In this way, groups provide feedback to other groups as they circulate among the models and compare answers. The instructor circulates, but can also stay close to those models with the most difficult questions. Keeping the groups small promotes participation, but groups may have to be combined into foursomes if materials are scarce.
5. Alternatively, this same format could be used to have the groups examine specific parts of a computer program and answer questions on a worksheet. One computer in a lab room could be used in conjunction with the crystal models; students could circulate among several computers or

workstations; or students could view other groups' answers and add their own answers using a shared file or directory.

6. With about 20-25 minutes remaining in class, the instructor has the groups review their work and ask each other about any of the flagged answers. After group discussion, the instructor gives an overview of the material covered and clarifies any remaining questions and misconceptions. Just before the class breaks up, the instructor asks each person to turn to a partner in the group and, "Tell the person one thing he or she did that helped you understand or learn something in lab, or that helped the group work well together."

Using formal groups for mineral identification activities to encourage positive interdependence

Any activity that is repeated regularly during a course, such as mineral identification exercises in mineralogy, is a good choice for cooperative learning groups. The example below is designed to help groups evolve higher-quality interaction through positive interdependence (Johnson et al., 1993). The students work toward a common goal of identifying minerals by their physical properties (goal interdependence); they share mineral specimens and tools for testing physical properties (resource interdependence); and they are assigned specific roles or tasks necessary to complete the assignment (role interdependence). Role interdependence is key in promoting cooperation; if students ignore their roles at first, the instructor should be prepared to step in and guide the group back to their role assignments in order for the group to work more efficiently and learn more. The roles are rotated among all students in the group so that each student has ample opportunity to handle specimens, test physical properties, and demonstrate concepts to the group. While roles can be rotated during a single class period, it is easier and less confusing for students to play a single role during class and rotate roles over the duration of the course. Alternative structures are suggested below, depending on class size and time constraints.

1. Students are assigned to groups of three. Each student within each group is given a card with the role assignment -- tester/presenter, fact-checker, or recorder -- and the student signs his/her name on the back of the card. (These cards can be re-used to distribute roles equally among all students). The recorder is given a datasheet prepared by the instructor for recording information about the properties of the minerals. The fact-checker should have a reference source ready, turned to the pages for the day's minerals. The tester/presenter is given a testing kit containing a glass plate, streak plate, etc. If the total number of students is not divisible by three, it is better to have one or two groups of two students, a tester/presenter and a fact checker/recorder.

2. In the first scenario, the total number of minerals to be examined for the period is divided among the groups so that each group has about 3-4 minerals. Within the group, the tester/presenter begins by describing a mineral specimen to the group, performing the tests and pointing out important characteristics. The other students listen carefully and ask questions. The fact-checker checks the information in the reference book while the student is presenting and makes suggestions AFTER the presenter is done. The recorder writes down information on the datasheet, noting questions or discrepancies. The process continues until all specimens are tested and described on the datasheet. A minimum of 15 minutes is needed for 3-4 specimens.

3. As an alternative, if you have many more or fewer students than specimens, divide the mineral specimens into stations spread out in the classroom. There must be at least as many stations as there are groups of students. Try to match the number of minerals at each station with the number of students in the groups; a maximum of 4 different minerals at any one station is good. If you have many more students than minerals to be identified, you may have multiple stations of the same minerals. If you have enough samples of those minerals with different habits, you can put multiple specimens of the same mineral at each station; if not, you can have students look at more than one station. At the station, the students play the roles of tester/presenter, fact-checker, and

recorder as in step 2 above. The process continues until all specimens are tested and described on the datasheet (about 15 minutes for 3-4 specimens).

4. Discrepancies commonly arise between stated and observed properties: for example, hematite and ilmenite samples may contain magnetite; the hardness of hematite may vary greatly among samples. Students may ignore the discrepancies at first(!); but having students play specific roles helps the instructor intervene and ask pointed questions, such as “Tester, show me how this hematite scratches glass,” or “Fact-checker, is ilmenite magnetic or non-magnetic,” or “Recorder, why did you write down red for streak when this streak is obviously dark brown?” In this way, the instructor can facilitate deeper questioning and learning.

5. Before moving on to a new set of minerals or a new station, each group reviews and discusses its minerals and highlights the MOST DIAGNOSTIC property(ies) on the datasheet.

6. Having the students obtain information about the remaining specimens can be handled in a variety of ways. For example, each group can examine all the specimens independently, either by rotating the sample trays among the groups, or rotating groups among the stations with different mineral specimens, at regular intervals (say, 15-30 minutes). Alternatively, the recorder can stay with the specimens during the rotation process and s/he can teach the new group about the minerals. The simplest and least time-consuming alternative is to have one person in each group (typically the fact-checker or recorder) present the group’s minerals to the entire class, listing only the most diagnostic properties. This has the dual advantage of enhancing accountability of the group members with more passive roles, and helping all the students to develop the ability to discriminate among properties and focus on the most important information. The recorder in the other groups writes down the information as it is presented.

7. It is very important to stress each student’s responsibility outside of the group work in class. For example, students have to review the entire set of minerals outside class time before any scheduled evaluation, and to prepare by reading the appropriate material in a reference text. Having the wrong information copied on a datasheet does not let the students off the hook!

8. For the last five minutes, the instructor asks students in groups to discuss the questions: “How did the assigned roles make the work more efficient?” and “What could the group do better next time?” While this is taking place, the instructor collects the datasheets and makes photocopies for everyone in the groups (or photocopies and returns the datasheets at a later date).

Using informal groups to promote active learning during mineral identification exams

Having students talk in a structured way during an “open exam” can encourage active learning during the evaluation process. This example describes an open exam on mineral identification. Informal student groups typically re-form every few minutes as students move among the specimens to be identified, but students can work entirely alone on the exam if they prefer. Individual responsibility is promoted by having students prepare “cheat sheets” in advance, and by grading individual exam sheets; there is no group grade for this structure.

1. Students arrive in class having previously prepared “cheat sheets” with information about the minerals. The cheat sheet is graded along with the quiz, and is typically worth around 10-15% of the total grade. The cheat sheet can be a 3 x 5 card, or a double-sided 8 1/2 x 11 worksheet.

2. The instructor has placed unidentified specimens around the classroom. Students circulate among the specimens, test the properties, identify the specimens, and fill out a worksheet listing the most important or diagnostic characteristics of each specimen. Students can talk among themselves and can refer to their cheat sheets. This allows the instructor to use complex specimens that challenge the students’ abilities.

3. There is an explicit "No Moocher" Policy (on the syllabus!) that gives the students autonomy: It is each student's responsibility to be prepared for the open exam; no student should feel obligated to help a student who is not prepared; and no one has the right to expect to be given answers. Students can escape "moochers" by simply moving to a different specimen.
4. Open exams typically generate a tremendous amount of discussion among students as they argue over the identification of the mineral specimens. The open format works best if repeated regularly over the course duration so that students become comfortable with the process. Students who "mooch" are quickly ostracized by the group and are easily recognizable to the instructor watching the quiz; such students simply stop mooching after one or two attempts.
5. When the students finish the quiz, they staple the cheat sheet to the exam sheet and turn them in. When all students have finished, the instructor goes around to each specimen and asks for the identification and properties. This takes 5-10 minutes and provides immediate feedback to the students so that any questions are quickly resolved.

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PHYSICAL PROPERTIES OF MINERALS AND DETERMINATIVE TECHNIQUES

An Introduction to Cooperative Learning

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How do you, as a student, make cooperative learning work ?

In a cooperative learning environment, you are responsible for others' learning as well as your own. I'm convinced that you don't really know something until you understand it well enough to teach someone else, a skeptical knowledgeable classmate, in this case. This learning strategy also reflects the reality that each of you has valuable insights and skills to contribute to the group. And by sharing, each of you will become better.

You will belong to one of several learning/teaching groups and assume part of that group's work load. Each group member accepts the responsibility of becoming an "expert" on part of the lab assignment. After completing your part of the assignment independently, you and "experts" on the same topic from other learning/teaching groups meet as an "expert group", to discuss your findings and to reach consensus. Upon returning to your respective learning/teaching group, each of you will teach (summarize and demonstrate on specimens) to your classmates what your expert group has concluded. The learning/teaching group has become a group (team) of different experts. Even though the original work was distributed, each student is responsible for all results. You are quizzed over all topics and those individual quiz scores become team scores by averaging. Each member receives the team score, so you have a vested interest in the performance of others in your learning/teaching group.

Some cautions: This environment only works when each of you puts a full effort into the small part of the total work assignment that is yours. Each member of an expert group must **critically review** the results of the other group members. **Expert group consensus must be based on proof - this week, by demonstrating a property on a specimen.** There is a tendency, in this week's lab particularly, to describe everything about your topic without critical analysis of just the most important aspects. In other words, don't simply regurgitate the text - which in this context does no one any good.

Instructions for this exercise

Read the appropriate sections of your text and the discussions in this handout. Use the reference specimens -- they should exhibit the behavior described in the text and this handout. If they don't, get help! Sometimes you may experience the limits and uncertainty associated with hand sample mineral identification; **don't hesitate to share examples of these uncertainties.** You will probably want to mention the location of good reference examples in your report to classmates. Text references are to Klein and Hurlbut (1993) *Manual of Mineralogy*, 21st edition (K&H).

→ Arrows mark demonstrations that you or a classmate will do and questions for which you must turn in answers.

Part A. Physical Properties Associated with Light

Read the explanations of **streak** and **luster** found on page 266 of K&H. Please take the time to study the reference specimens of those minerals cited as examples for luster types and use terms properly in your report to classmates.

Although sometimes obvious, **metallic** and **nonmetallic** lusters can be very difficult to distinguish from one another. Dark minerals (black, brown, deep green) appear to be opaque (metallic), although on their thin edges they are slightly transparent (and therefore nonmetallic!). You could ask the instructor to loan you a thin section of a seemingly-opaque, dark, nonmetallic mineral for which you have a handsample that shows the effect described above. Metallic minerals commonly develop a tarnished outer surface that masks the true luster, until scratched.

Luster is the appearance of the mineral's fresh surface in reflected white light. Although luster describes the reflected component of light, a quantitative relation exists between the **index of refraction (n)** (see K&H page 290) and the type of luster displayed by transparent or translucent minerals (see Figure 6.13, page 260 in K&H). An example of each species in italics below is available for your use as a reference. Non-metallic lusters:

adamantine splendent = $2.6 < n < 3.4$ (*orpiment, cinnabar, hematite*)
adamantine = $1.9 < n < 2.6$ (*diamond, cerussite, anglesite*)
vitreous = $1.3 < n < 1.9$ (*quartz, tourmaline, 70% of minerals*)
resinous = $1.9 < n < 2.6$ (*sphalerite, sulfur*)

Some non-metallic lusters are produced by physical optical effects:

pearly = mineral with internal microscopic separations parallel to its surface
(often cleavage separations) - *talc*
greasy = mineral with a thin outer film of altered material of different n than the fresh material underneath. *nepheline* is the best example.
silky = mineral with parallel micro-fibers. *chrysotile, fibrous gypsum, malachite*.
play of colors - from optical interference. (see K&H pages 266-267)
opalescence (*opal*)
iridescence: schiller
labradorescence (*labradorite = plagioclase feldspar*)

Metallic lusters, usually are assigned to one of three subtypes - submetallic, metallic, or splendent. The percent reflectance of these mineral surfaces, as measured by sensitive photometers, provides quantitative measures of luster. "Metallic" surfaces range between "submetallic" (at low reflectance) and "splendent" (at high reflectance) lusters. Mineral examples for **submetallic** (8-20% reflectance) include: *magnetite, graphite, chromite*. Minerals with **metallic** luster (20-50% reflectance) include: *molybdenite, galena, chalcopyrite, bornite*. Minerals with **splendent metallic** luster (50-95% reflectance) include: *pyrite, marcasite, fresh copper or silver, gold, platinum*.

- For the samples provided, describe the **luster and streak**.
- For the samples provided, estimate the **% reflectance** by comparison to standards.

Part B. Breakage Behavior - Cleavage, Fracture and Parting (K&H pages 252-254)

Cleavage, fracture and parting describe the appearance of broken mineral surfaces. When a mineral breaks along flat planes, it has **cleavage** or **parting**; when the broken surface is irregular, the mineral displays **fracture**. Some minerals display cleavage and fracture, others have only one or the other. Fracture, cleavage and parting are detected by rotating the specimen so that it reflects light to the observer's eye and by simultaneously judging the flatness and perfection of the reflecting surface. Several terms describe the *quality of cleavage*:

perfect - it is difficult to break the mineral in any other direction. Cleavage surfaces are smooth and extensive. (*galena, calcite*)

good - breaks easily along cleavages but can also be broken in other directions. Cleavage surfaces are smooth but are interrupted by other fractures. (*enstatite, orthoclase*)

imperfect - breaks somewhat more easily along cleavage surfaces than along other surfaces.

Cleavage surfaces tend to be small and much interrupted. (*diopside, beryl* {0001})

Fracture is described as **conchoidal, fibrous, splintery, hackly, irregular** or **uneven**.

Some hints for the careful observer: Breakage can be described only when individual crystals are large enough to be seen (many minerals occur as aggregates of tiny individuals). The description of breakage in minerals is also complicated when the observer must distinguish between broken surfaces and crystal faces. Crystal faces are perfectly smooth. Cleavage surfaces exhibit "sheeting" or "stepping" parallel to the cleavage plane. Transparent minerals show incipient cleavage breaks that look like flat ghosts, inside the mineral, parallel to the cleavage on the surface of the specimen. These incipient internal breaks are responsible for the "play of colors" seen when light reflects from the perfect cleavage surfaces of some minerals (cf. *calcite* and *fluorite* examples in the lab).

→ For the samples provided, record the "quality of cleavage" and "type of fracture."

Examine several samples of *corundum*. Note that some samples exhibit "cleavage" yet others do not. Therefore, this "false cleavage" (only present on some samples of a mineral) is an example of **parting** (cf. K&H Figure 6.5b).

In addition to recognizing the presence of cleavage, one should determine the number of **cleavage directions**. Each direction might be responsible for several parallel flat broken surfaces on a specimen. Alternatively, one could count the sets of parallel "cleavage traces" that intersect the specimen's surface. These traces are the intersections of breakage surfaces with the surface being viewed by the observer (cf. hornblende cross section, K&H page 490). When more than one direction of cleavage is present, one must describe the angle between the sets. The combined data about number of directions and angles between them can be expressed by the descriptive terms shown by Figure 6.4 in K&H (page 253) or by specifying them as follows: "2 directions intersecting at 56° and 124° to one another", for the amphibole example on page 490.

→ For the samples provided, record the **number of cleavage directions** and use a contact goniometer to measure the **angle** between directions.

Part C. Hardness (K&H pages 254-255)

Mineral **hardness** is usually described by comparison to the ten minerals in the Mohs scale of relative scratch hardness. Alternatively, hardness may be estimated for soft minerals by using a

[What follows is a reply from one mineral scientist to an Internet request for references about mineral toxicity. Read Puffer's paper, this note and reach your own conclusions.]

Date: Tue, 21 Mar 1995 15:10:27 -0500 (EST)

From: Malcolm Ross, U.S. Geological Survey

Subject: Mineral Toxicity, a paper by J. H. Puffer, Mineralogical Record., Feb. 1980.

Pete Modreski recommended this paper as a reference on the subject of minerals and health. If those teaching mineralogy wish to scare the hell out of their students, let them read this paper. Afterward they'll probably change their major to something non-controversial like fly tying. Puffer's Table 1 lists nearly 200 minerals that are "analogous to minerals described by NIOSH (1977) as suspected or proven toxins." One is hard pressed to understand how most of these minerals got on the toxic list, except to note that the NIOSH people know nothing about mineralogy.

Barite, one of the most insoluble minerals, is ingested as a barite slurry for medical diagnostic purposes. **Corundum, native gold, beryl, brookite, and hematite** are extremely inert minerals and are in no way toxic unless, perhaps when ground up as sub micron particles and inhaled in large quantities. Did you know **calcite** is a toxic mineral? I'll bet not! This list is so ridiculous that it defies intelligent comment. One does not place minerals in their mouths, especially the soluble minerals, the same way one does not ingest reagent chemicals from your chem lab. All chemicals are poisonous when taken in sufficient amounts and all minerals dusts are dangerous in large quantities. **Hexavalent chromium salts** are dangerous in certain situations; **trivalent Cr** in minerals is unavailable biologically, the same way lead-bearing minerals in mine wastes are unavailable biologically. **Lead-bearing minerals** when ingested they go right through the digestive tract in a few hours before any significant dissolution takes place. Children in old lead mining towns, such as Leadville, CO, who played on lead-bearing mine tailings show blood lead levels that are no higher than the U.S. average. Yet the fear of lead in the environment of these towns has devastated real estate values. I could go on and on about this subject, but can only plea that mineralogists get a better understanding of health risks by very carefully reading the primary medical literature instead of relying on second hand literature promoted by fear mongers.

Comments to the Instructor

This laboratory exercise builds on learning from a prerequisite course (Physical Geology) and therefore works well early in my mineralogy course. I use it before crystallography, which explains why Miller indices and form names are not used to describe cleavage. Many of the students in my course have not yet had chemistry and are still developing basic skills in careful observation. Many are still learning the importance of quantitative ways of describing nature in contrast to the more qualitative ways that minerals and rocks are commonly handled in introductory geology courses. The topic is one about which they have some knowledge and are, therefore, in a comfort zone as they learn the "Jigsaw" cooperative learning strategies. This activity also demonstrates the limits and uncertainty associated with hand sample mineral identification as a context for the more quantitative techniques introduced later in the mineralogy course and later still in petrology, etc.

This laboratory is keyed to Klein and Hurlbut's Manual of Mineralogy (21st Edition, John Wiley & Sons). It could easily be adapted to another text of equal rigor and thoroughness. My syllabus explains the text's role as "... an excellent shelf reference on crystallography, crystal chemistry, and determinative mineralogy. Use it as such this semester. The text also provides a framework for advanced rock classifications you will encounter in geology courses. It is the primary data source you will need this semester for laboratory and homework exercises." Critical reading of the text by the student replaces lectures on some topics. Some of your students might benefit from reading excerpts from Bloss, F.D. (1971) Crystallography and Crystal Chemistry, an Introduction (Reprinted 1994, Mineralogical Society of America), Chapters 11 & 12 or Frye, K. (1993) Mineral Science an Introductory Survey (Macmillan), Chapter 4.

The "Jigsaw" pedagogy upon which this lab is based also provides the environment for four succeeding labs in which the students learn the megascopic characteristic properties, chemical composition, and a geologic significance for each of approximately 100 minerals. A good discussion of the technique appeared in The Journal of Geological Education (Constantopoulos, 1994, vol. 42, 261-3). See also Srogi and Baloché (this volume). I have used the technique three times and am convinced of its value. Every student is active and focused through the entire lab period, each improves his/her skills in oral presentation in small groups, each improves his/her skills in careful observation and analysis of specimens. The later benefit seems to be associated with a perception by the students that they can afford to be more careful and observant because each has less work to do than if they each completed the entire exercise individually. They also seem to understand and accept the responsibility each assumes for their classmates' learning. During the cooperative learning laboratory sessions, the instructor serves as arbitrator when members of an expert group can not agree or seem to be totally off track. Often I refer them back to the critical passage in the text rather than giving them "the answer". The instructor as ultimate authority (giver of truth) is replaced by the instructor as guide (which may require restraint on your part !).

One of the instructor's challenges is organizational, creating enough learning/teaching groups so that each of the four parts (A-D) of the exercise is completed by an expert group with between two to four students. Part B can be divided among two people yielding five topics (expert groups), if that number better accommodates your class. Consequently, this exercise accommodates between eight (2x4) and twenty(4x5) students. I commonly distribute students randomly among the topics until all have a task for the individual study phase and no topic (expert groups) has more than four students. There is no advantage to having all expert groups the same

size, so don't worry if unequal groups arise. However, you should divide groups larger than four into smaller expert groups with the same topic. You could drop the density part from the collaborative strategy (let every student do it) for sections with six students. Large lab sections with multiple expert groups on the same topic should be allowed extra time for those expert groups with the same topic to present their conclusions to one another before members return to their learning/teaching clusters. I use the performance of each student on this first, rather-straight-forward activity to guide my selections for the learning/teaching groups who will remain together throughout the next four to five labs on systematic mineralogy.

A second major challenge for the instructor is monitoring the pace of activities so that all expert groups finish in a timely manner and near the same time. There is a real advantage to giving time limits for the individual work (perhaps 30-45 minutes), the expert group conferences (30-45 minutes), and ample time for each expert to teach others in his or her learning/teaching group. This laboratory activity is designed for three hours. One could give the individual assignments a day or two before the lab sessions and expect the students to come to lab having read the appropriate portions of the text, thus saving some of the time allocated for individual work. Unless the instructor monitors the pace of work, the students tend to prolong each activity or drift toward social conversations in the group activities.

Each student is graded on the total lab report, his or her original work and that of classmates. If experts present wrong information, all who accept that data are penalized. This strategy reinforces the learner's responsibility to ask constructive questions of experts when the information doesn't make sense. Each student can also be graded individually on the portion of the exercise for which she was responsible. Once students accept their mutual dependence and stop competing with one another, the class room atmosphere becomes very supportive.

A list of the samples I use is included. There are enough of each so that each expert has representative material for demonstration during the final learning/teaching sessions. The lab room also contains sets of reference samples representative of the Mohs hardness, luster, fracture, cleavage and specific gravity examples mentioned in the lab instructions and text.

Many of the qualitative techniques upon which this exercise is based are supplemented later in the semester by more quantitative techniques. Most of my students don't develop the skills and self-confidence necessary for the quantitative methods until later in the semester. Which of the following techniques you may choose to include will certainly depend on equipment available and appropriate problems in subsequent lab exercises. There is real value in connecting topics between labs so that students can not compartmentalize their learning and avoid the connections among topics that we all strive to build into our syllabi.

Luster: measure indices of refraction in oils with polarizing light microscopes, measure reflectance by microscope photometry.

Cleavage: measure cleavage angles of several amphiboles and pyroxenes in thin section.

Hardness: measure microindentation hardness.

Specific gravity (heft): measure density by immersion or by pycnometer.

Color: determine quantitative color coordinates from spectral reflectance; compare to Munsell color charts.

Later in the semester, in the context of solid solution series, the students compare systematic variation of physical properties (density, color, index of refraction) and chemical composition for garnets and olivine group minerals. One could also include variability of cell edges if XRD analysis is an option. The chemical data is collected on a SEM-EDS system from the same samples used to determine density, color, and index of refraction in the earlier lab exercises. This solid solution lab also provides topics for homework problems on calculating theoretical density, crystal chemical rules for atomic substitutions, recasting chemical analyses to mineral formulae, and causes of color in minerals.

My choices for unknown specimens in this first Physical Properties lab:

Luster & Streak

black tourmaline crystal
sulfur - massive
barite crystal
calcite crystal
celestite crystal
bornite with covellite coating

% Reflectance

chalcocite
goethite
gold
ilmenite
wolframite

Density (heft)

feldspar (softball size)
galena (golf ball size or smaller)
celestite (golf ball size)
cerussite (golf ball size)
quartz (golf ball size)
lepidolite (silver dollar size)

Quality of Cleavage & Type of Fracture

chalcocite - massive
chalcopyrite - massive
quartz
copper
garnet - massive
garnet - with parting
galena
anthophyllite
tourmaline

Cleavage Directions & Angles

fluorite - cleavage octahedron
calcite - cleavage rhombohedron
gypsum (selenite)
mica
augite
stibnite
calcite (broken crystal with cleavage and crystal faces)
plagioclase
galena
hornblende
halite - cleavable
fluorite - intergrown coarse
sphalerite - cleavable
dolomite - cleavable

Scratch Hardness

quartz
apatite
gypsum
feldspar
pyrite
fluorite
calcite
corundum
talc
chalcopyrite

Physical properties reference sample sets are sold by:

D. J. Minerals, P.O. Box 761, Butte, Montana 59703-0761, (406-782-7339).

Omni Resources, 1004 S. Mebane Street, P.O. Box 2096, Burlington, North Carolina, 27216 (910-227-8300) (<http://www.omnimap.com>).

Watkin's Mineral Corp., 117 Pembroke Lane, Wichita Falls, Texas, 76301-2929.

Ward's (1-800-962-2660) (<http://www.wardsci.com>).

Other equipment: contact goniometers, equipment for measuring specific gravity.

MINERAL CLASSIFICATION—WHAT'S IN A NAME?

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*"The purpose of classification is not to set forth certain and final truths,
but rather to be used as stepping stones towards greater understanding."
L.C. Graton*

Objectives: This is an introductory exercise that is designed to 1) help students develop their observational, descriptive, and interpretive skills; 2) place mineral classification schemes in a rational context based on the students' observations as well as a historical perspective; 3) prepare students for more detailed coverage of material by encouraging them to "be scientific" and 4) demonstrate effective teaching practices using a constructivist approach, collaborative learning, and peer assessment. This exercise can be used as an "ice breaker" early in the course to encourage students to get to know each other and to work together, to become familiar with determinative tests that will be used throughout mineralogy, and to allow the instructor to observe "baseline" student performance as an aid in planning future activities to better address student needs. Additional notes for instructors are keyed to the text. (Notes 1 and 2).

Background: Students should be familiar with basic determinative mineralogy: hardness, cleavage, general crystal forms, luster, color...things that can readily be observed in hand sample (see exercise by Ken Bladh, this volume). If students are not familiar with these properties, they should be encouraged to review this material from introductory texts, or better yet, sets of minerals that display these properties. (Note 3).

Materials: Sets of common rock-forming minerals should be provided which display the breadth of physical properties that can readily be observed in hand sample. Use whatever minerals are readily available from your collections. However, two features should be built into the teaching sets: 1) include numerous varieties of the same mineral (e.g. terminated quartz crystals, massive quartz, smoky quartz, chert; rhombohedral calcite, dogtooth spar, etc.), and 2) numerous minerals that have the same crystal form (e.g. cubic pyrite, galena, halite; prismatic amphibole, tourmaline, etc.). Twenty to thirty different samples can be used, depending on materials available and amount of time that can be allotted to this exercise. (Note 4). A suggested list of minerals would include:

pyrite	galena	halite	marcasite
calcite (rhom)	calcite (dogtooth)	gypsum (selenite)	chalcopyrite
quartz crystal	massive quartz	smoky quartz	sphalerite
plagioclase (with twins)	microcline/orthoclase	kaolinite	magnetite
olivine	hornblende	tourmaline	biotite
pyroxene	hematite (red, earthy)	hematite (specular)	muscovite

Assignment: Develop a classification system that will differentiate and organize the members of the “mineral kingdom”. Use the physical properties you can observe in hand sample to develop the criteria for organizing your classification system. Your system must have the following characteristics:

- 1) the system must be expandable, so that you can use it to classify new minerals that may be discovered;
- 2) the system must be reproducible, so that other scientists can use your criteria to come to make the same interpretation about mineral classification that you have originally determined;
- 3) the system must be easily applied by other workers who will need to use it effectively in the field or in the lab.

Work in small groups (3-4) to develop your classification system. You will have to come to a consensus about which properties should have the highest priority, which properties are useful for general discrimination of minerals, and which properties may be diagnostic of specific minerals. (Note 5). Your final product should be a taxonomic “tree” with a written description of how to systematically use your procedures to classify minerals. (Note 6).

THERE IS NO “RIGHT” ANSWER. However, you should be prepared to justify your reasons for selecting the order of the criteria for your classification system. As a starting point, you may want to develop a series of “yes or no” types of questions; e.g. is it metallic, is it soft, etc. You will encounter some difficulties and apparent contradictions as you develop your system. For further insight into this problem, read the article by Robert Hazen, “Mineralogy: A Historical Review” (Journal of Geological Education, 1984, v. 32, p. 288-298). How can you use the observations, interpretations, and arguments of the “formalists” vs. the “naturalists” to revise your classification scheme? (Note 7)

Reflection: (Note 8)

1. What problems were encountered by early scientists who believed that “form and only form should be used for the classification of minerals”?
2. What problems were encountered by early scientists who developed classification systems based on “empirical” or natural properties of minerals?
3. What was the contribution of James Dwight Dana to the problem of mineral classification?
4. What physical properties used in your classification scheme are qualitative and which are quantitative? What are the benefits and limitations of each type of observation?
5. What can the physical properties of minerals tell you about fundamental principles in nature? (e.g. structure and composition of minerals, etc.). Based on your observations, what other information would have helped you develop your system? How could you have obtained this information?
6. Historically, what technologies became available that brought new evidence to this controversy? What new evidence became available to address the physical and chemical properties of minerals?
7. What technologies are currently available to aid with the identification and characterization of chemical and physical properties of minerals? (Note 9)

Assessment: (Note 10)

Trade your classification system and “user’s guide” with another group. Each group should then assess how effective the classification system is. Pick out a number of representative samples and use the system to see if you get the same answer as the original group. Did you run into difficulties in making decisions about the properties of some of the minerals? Take a new mineral (provided by your instructor) and see how this system works for a new material? Is this system internally consistent (i.e. you get the same answer for the same types of minerals)? Is it easy to use? Provide constructive advice on problems you may have encountered, and provide some suggestions on how you could solve this problem. This is not a grade--it is meant to be an informative review that allows you to help your colleagues better perform their tasks.

Notes for Instructors:

1. Cognitive psychology has demonstrated that there is a hierarchy of developmental skills that include observation, description, interpretation, and integration in the progression of higher order-reasoning. This exercise presents an opportunity for students to exercise their observational skills, to confront the need for precise description of natural phenomena, and to begin to interpret their observations towards an organized understanding of the natural world.
2. This exercise is built upon the underlying principles outlined in Project 2061 Science for All Americans (AAAS, 1989). In particular, Chapter 12 makes recommendations about “Habits of Mind”: curiosity, openness to new ideas, skepticism, observation skills (keep a notebook that accurately describes observations made, use appropriate instruments to make direct measurements), communication skills (express orally and in writing the basic ideas covered, be comfortable and familiar with standard vocabulary, organize information, participate in group discussions...), and critical response skills (logical conclusions from evidence, use of analogy, discrimination of fact and opinion).

Chapter 13 (Science for All Americans) addresses “Effective Learning and Teaching”: what students learn is influenced by their existing ideas, progression in learning is usually from the concrete to the abstract, people learn to do well only what they practice doing, effective learning by students requires feedback, and expectations affect performance. Specific recommendations for improving learning activities include: start with questions about Nature, engage students actively, concentrate on the collection and use of evidence, provide historical perspectives, insist on clear expression, use a team approach, do not separate knowing from finding out, de-emphasize the memorization of technical vocabulary, welcome curiosity, reward creativity, encourage a spirit of healthy questioning, avoid dogmatism and present science as a process not as unalterable truth.

The recent review of undergraduate science education, “Shaping the Future, New Expectations for Undergraduate Education in Science, Mathematics, Engineering, and Technology” (NSF 96-139) calls for, “All students have access to supportive, excellent undergraduate education in science, mathematics, engineering, and technology, and all students learn these subjects by direct experience with the methods and processes of inquiry.” The most important component of successful research and educational activities lies in the process of discovery, and students should be given every opportunity to discover fundamental concepts and principles in their regular coursework.

3. All students will come to class with preconceptions or misconceptions about the subject, usually based on limited personal experience. When presented with new information, most students will attempt to append this new material onto their own incomplete or inaccurate understanding of a subject, rather than coming to a true understanding of the subject. The basis of a constructivist approach is that students should be given the opportunity (required) to discover inaccuracies in their own understanding, and to “construct” a new understanding based on a more appropriate interpretation. For example, confusion about planar surfaces that may either be a crystal faces or cleavage planes is the type of problem that plagues many students. By working with numerous examples of different types of cleavages and crystal forms, students should be able to determine for themselves the criteria needed to distinguish these features.
4. Ambiguity is purposefully built into this exercise so that students will confront a) natural variation which they can expect in the field, and b) the historical dilemma encountered by mineralogists and natural scientists up until the time of Dana. This historical development will be further discussed below.
5. Collaborative learning is an effective way to get students to formalize, articulate, and defend ideas. There is a wealth of literature that describes the effective use of collaborative learning (see contribution by Srogi, this volume). And most of us do collaborative science, so the students should get used to doing science in this mode.
6. Similarly, there is an extensive literature on the use of effective writing practices in science education. It is essential that students come to value clear and concise writing as part of their pre-professional training.
7. Revision is an important component of constructivist approaches, as students are informed by new information from either direct observation, or from other sources (such as earlier literature)
8. In the “learning cycle”, four elements for effective learning are identified: individual and/or group planning; concrete experience and observation; considered reflection on the experience with synthesis and abstract conceptualization; and testing of newly developed concepts in new situations. Of these components, the reflective stage is often omitted--students typically finish an exercise without further consideration of how the results relate to earlier experiences, other bodies of knowledge, or future implications.
9. This question will help make connections to the current situation in mineralogy--and will set up a transition to other units that will cover crystallography, crystal chemistry, etc. In particular, it will help students see the context of what we think we know, and how we can determine/measure/analyze minerals to reveal fundamental properties.
10. Peer evaluation continues the learning process, helps to transfer some of the responsibility for class activities to the students, and relieves some of the burden of the instructor. However, the guidelines for evaluation must be clearly established. The first and most important rule is that *ad hominem* attacks on other students will not be tolerated. It should also be made clear that the evaluation is of the product not the person. My experience has been that my students have been brutally frank and honest in their evaluations. Students have little patience (less than my own) for sloppy work that wastes their time. Peer evaluation is part of our professional life, whether in academics, industry or government, and students should be made to feel comfortable about the need for review and revision of their work.

You may want to use both an internal and external review of the work--the external review would be of the project itself conducted by another group to determine the effectiveness of the classification schemes. The internal review could be made by the members of a given group to evaluate the contributions made by each team member. It is also worthwhile to periodically ask students to do a personal review, to see what they feel they contributed to and learned from the project.

This type of project also allows the instructor to do his/her own audit of the students at the start of the course. Part of "student-centered learning" is to become aware of the strengths, weaknesses and preferences of each student. Informal observation of the students working in groups will help to give you an idea of which students are leaders, who prefers to work alone or in groups, who has an aptitude to be analytical or synthetic, etc. This type of baseline data for your class can give you valuable information on how to adjust subsequent exercises to reinforce the strengths of some students, and to help design activities that can address other weaknesses (i.e. this provides the basis for "formative" evaluation of class activities for the rest of the term).

11. This exercise presents a historical perspective, as students see that the classification system we use is the product of a long evolution of contributions. It also demonstrates that students can be part of this continuum. Perhaps the most important lesson is that classification itself is not the ultimate goal of a course in mineralogy, although it is a necessary and requisite step. The properties we observe in minerals are the manifestations of other fundamental principles of Nature, and through detailed study of minerals we can find out more about the way the world operates. As Calvin said to Hobbes in his final frame: "Let's go explore..."
12. When I have used this exercise on previous occasions, I found that about 75% of the students tended to adopt the "natural history" mode of classification, and about 25% adopted the "crystal form" mode. Nature or nurture? I think that there may actually be some "born" crystallographers out there! If you adopt or adapt this exercise, I'd be interested in knowing if you notice a similar bifurcation of approaches among your students.

A TERM-LONG MINERALOGY LAB PRACTICAL EXAM

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Overview

One of the hardest things to teach in mineralogy is the ability to identify minerals in hand sample. I think this is principally because mineral identification is a skill that, in large part, must be learned by long practice.

For several years I used the standard “rocks in a drawer” approach to teaching hand specimen identification. This involved handing out a list of important minerals and reviewing drawers of teaching samples in lab by going over the individual mineral properties and some aspects of their crystal chemistry and structure. For the lab exam at the end of the course students were required to identify a portion of the minerals seen in lab. This method was largely unsuccessful, in part I think because the students had no tangible goal to work toward. The goal of learning to identify the minerals on the list is too amorphous, since it does not refer to a specific set of specimens or properties but rather to an unknown set of test specimens that may differ widely from the practice specimens. As a result, students have no clear idea of what properties are important, and therefore don’t know when they have studied enough or if they have studied the right things. When faced with such uncertainty, many students tend to do too little rather than too much. An additional problem with final exam-oriented teaching is that the students do not develop skill at using advanced methods of mineral identification such as X-ray diffraction and mineral optics. Although individual lab exercises can cover X-ray diffraction and other mineral identification techniques, it would be worthwhile for students to practice using them repeatedly as practical problem-solving tools.

To address the problems with final exam-oriented teaching of hand specimen identification, I decided to change my goals:

- 1) Mineralogy students do not need to be able to identify most minerals presented to them in classic mineralogy courses. A relatively small subset of minerals, including important rock-forming minerals, is sufficient for most geologically-related employment and graduate school. More obscure minerals can be learned on the job.
- 2) Mineralogy students do need to learn the tools and skills of mineral identification. These include determining the usual properties hardness, luster, color, streak, and so on, and more advanced techniques including density measurement, mineral optical properties, and X-ray diffraction.
- 3) Mineralogy students should practice these techniques many times on a variety of samples. I do not, however, require them to determine every property for every specimen, since this involves a lot of unnecessary repetition that annoys students.
- 4) Students should have an obvious goal for their mineral identification exercises and, at least minimally, to have a stake in reaching the goal other than their final grade. I hope that this increases student motivation.

On the first day of mineralogy class each student receives a box of 65 thumb-sized, numbered mineral specimens, which are theirs to keep. All of the minerals are described in their text (Klein and Hurlbut, 1993). At the end of the term students must turn in a list of their 65 identified minerals, with the properties they used for identification. Because students keep their samples, most really do want to learn what they are, and they have an incentive to test the samples carefully without destroying them, just like a geologist would (or should). One twist to letting the students keep the minerals, suggested by Michael Wolf, is to let students keep only samples they correctly identify. This apparently increases their incentive to work hard. Although the sample sets can be expensive (about \$20 each), our teaching collection receives much less damage than previously.

I still go over the practice specimens in lab, but I dwell much more on common rock-forming minerals, the reasons for variability of mineral properties, and on crystal chemistry, crystal structure, and the origin and uses of minerals. I encourage students to bring their box of samples to lab to compare them with those in the teaching collection. After all, that is frequently what real geologists do. It is also a useful learning experience since relatively few of their samples really look like their counterparts in the teaching collection, and some specimens that look similar are actually completely different minerals. Students quickly learn that direct comparison is an easy way to identify a few samples, but does not work for many.

Discussion

In several respects my redesigned mineralogy lab has been extremely successful. Most students love their samples and work hard outside of class to identify them. They usually identify several within a few minutes of opening their box on the first day (e.g., quartz crystal, muscovite, biotite, and halite), based on previous geology classes and other experience. This gets them started and makes them realize that the goal of identifying all of them is attainable. Early in the term I review all the mineral identification techniques available in our department, including X-ray diffraction and basic practical optical mineralogy using grain mounts. By the middle of the term the students have all the necessary tools and they usually start working in earnest. It is wonderful to come in late in the evening and find several students working on their mineral sets; something I never saw with the old method. The students generally get quite skilled with the identification techniques that we cover, except, alas, for optical techniques. Students quickly learn that the flashy computer-controlled XRD can be a slow and tedious way to identify minerals, and so most use it as a last resort (I disable the automatic peak matching program to encourage students to use their brains rather than a machine, which in any case is often wrong).

Although I would never return to my old ways, there is a problem with the redesigned labs. Students become relatively skilled at mineral identification, but still do not really learn to identify mineral specimens by sight or with a few tests even for most of the common rock-forming minerals. I have partly remedied this problem by putting out a weekly "puzzle box", each of which includes, among other things, five unlabeled common rock-forming minerals that students will be expected to know for the final exam. Since these samples help them to identify their own samples, the fact that the "puzzle box" is optional does not seem to hinder the students from looking and learning from it.

In summary, giving students their own box of minerals to identify during the entire term gives them a clear and tangible goal, motivation to work and learn, lots of practice looking at samples using various identification techniques, and practice interpreting diverse and sometimes conflicting data. In addition, students develop a camaraderie as they voluntarily work during evenings and weekends. Since students do this willingly, they really have fun even if they do complain a bit. Most students end up successfully identifying about 80% of their samples, 90%

if you include identifications that are wrong but are very similar to the actual minerals. I admit that many of the minerals I give them are quite difficult to identify, but that's fine.

My favorite mineral in the set is romanechite (formerly psilomelane), a hydrated Ba-Mn oxide. It looks rather like an iron oxide or dense hydroxide, but the various basic properties are conflicting when one tries to identify it as an iron mineral. As a last resort, students try X-ray diffraction and find out, to their horror, that it is X-ray amorphous! However, when they read their book carefully, they do indeed find that romanechite is X-ray amorphous, and most identify correctly.

Mineral List

The following is the list of minerals that we currently use. The list changes yearly as different minerals become more or less expensive or available. Some minerals are present in two or more varieties. The samples are numbered differently for each class, and the students do not get this list.

Actinolite	Chromite	Kaolinite	Satin spar
Alabaster	Corundum	Kyanite	Selenite
Albite	Diopside	Labradorite	Serpentine
Amblygonite	Dolomite	Lepidolite	Siderite
Anorthoclase	Dumortierite	Limonite	Sillimanite
Apatite (chunk)	Enstatite	Magnesite	Sodalite
Apatite (crystal)	Epidote	Magnetite	Sphalerite
Asbestos	Fluorite	Microcline	Spodumene
Barite	Galena	Muscovite	Talc
Bauxite	Garnet	Olivine	Tiger eye
Beryl	Glauconite	Opal	Topaz
Biotite	Goethite	Phlogopite	Tourmaline
Calcite	Graphite	Pyrite	Travertine
Celestite	Halite	Quartz crystal	Wollastonite
Chalcopyrite	Hematite	Romanechite	
Chert	Hornblende	Rose quartz	
Chrysocolla	Jasper	Nepheline	

Reference

Klein, C., and Hurlbut, C.S. Jr. (1993) Manual of Mineralogy (21st edition). John Wiley and Sons, Inc., New York, 681 p.

TAKE HOME LAB EXAM: INSTRUCTIONS TO STUDENTS

You have been given a box of 65 mineral specimens, and these are yours to keep as a souvenir of this course. These specimens are the take-home part of your lab practical final exam. You are to identify all 65 specimens. Some of the specimens are pure minerals, others are impure minerals, and others are mineraloids or even rocks. There may even be a few duplicated minerals. All of the minerals are in your text.

I will not give any help identifying these specimens, except to clarify the instructions, to help with analytical and identification techniques, and to point out which mineral is the important one in a sample. You are to work independently and may not help each other except with identification techniques. You can use any of the mineral identification techniques available in the Geology Department (except ICP-MS analysis) including:

Hardness	Reaction with acids
Color	Streak
Cleavages and cleavage intersection	External crystal form
Stereo microscope or hand lens	Density
Taste	X-ray diffraction
Mineral optics in immersion oil	Fluorescence under U.V. light
Radioactivity (Geiger counter)	Comparison with known minerals

I recommend against relying heavily on visual comparison of your unknown minerals with specimens in lab or in the display cabinets. Outward appearances can and will be misleading! It is more reliable to base your identification on several properties. Full credit will be given only for properly identified minerals with a sufficient and accurate set of identifying characteristics. Extra credit will be given for chemical and structural data that *you* determine (give data), for variety names, and for any other pieces of interesting information that you can determine. Feel free to use any resources in the lab, in the library, or on the Internet.

Hand in the following information in table form:

Mineral Name: The basic mineral name and/or variety. This is the name of the most abundant or prominent mineral in the specimen.

Distinguishing Characteristics: Give the characteristics of this specimen that you determined and used to identify this mineral and its variety. This can be just a few properties if it is that obvious, or several properties such as hardness, color, streak, X-ray pattern (give specific peaks and positions used for identification), crystal form, mineral optics (give refractive indices, optic sign, 2V, etc.), density (give measured value), and anything else.

Other Information: Give any other information that is important, including other minerals that occur in the specimen, other properties not listed under Distinguishing Characteristics, chemical composition as derived from X-ray pattern, density, or mineral optics, crystal form, twinning, etc.

FIELD NOTES

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*The Earth never tires,
The Earth is rude, silent incomprehensible at first,
Nature is rude and incomprehensible at first,
Be not discourag'd, keep on, there are divine things well envelop'd,
I swear to you there are divine things more beautiful
than words can tell.*

Walt Whitman
Song of the Open Road

Field trips are commonly the most memorable educational experiences for many students, and serve as excellent mechanisms in the recruitment and retention of students in geology programs (e.g. McKenzie et al., 1986; Karabinos et al., 1992). Field trips provide the opportunity for students to become motivated to learn, and participation on field trips results in measurable impacts on student values (sense of importance), interests, and attitudes (sense of enjoyment) about the subject matter (Kern and Carpenter, 1984). Field trips help us to experience the joy of working in a natural environment, the excitement of discovery, and the satisfaction engendered by mastery of content and increased appreciation for the methods of scientific investigation. At the same time, I'm sure we have all experienced field trips from hell on which students were ill-prepared to undertake the field trip activities, on which field trip "activities" degenerated into monologues by leaders that limited direct participation, on which litanies of names and places were presented out of context, on which activities were prescriptive and precluded exploration and discovery, on which participants were forced to endure death marches (or equivalent feats of physical heroism), or on which extreme personal discomfort was the result of lack of preparedness for the extant conditions or poor logistical planning. Due to the central role of field experiences in many geoscience curricula, it is fair to ask how we can ensure that field trips are optimal experiences for students--for learning and for personal development. Beyond the shared social experience and perhaps relief from routine coursework (there is some justification for fun, social outings), the question of overall effectiveness of field trips as educational activities must be addressed. Although there is not a large literature that speaks to this question (most of it derives from studies of K-12 field trips, not necessarily specific to geology), there are some clear indicators that have emerged about the characteristics of field experiences that are most effective for student learning.

The most important role of field trips in the learning process is in "direct experience with concrete phenomena and materials" (Orien, 1993). The very nature of field trip exercises requires students to be active learners, rather than merely covering material in a passive mode in a traditional classroom. Furthermore, experiential activities facilitate the transition from lower-order learning strategies (e.g. memorization of information) to the higher cognitive learning strategies required to master and retain abstract concepts (e.g. MacKenzie and White, 1982; Orien, 1993). Kern and Carpenter (1986) have shown that lower-order learning is virtually identical for all students whether or not they have participated in field experiences. However, they found that field experiences enhanced students' ability to understand, analyze, synthesize, and use acquired information and concepts. It is best to incorporate field trips in the early "concrete" part of a course, providing materials and contexts that can form the basis for future development of abstract concepts, and offering activities that cannot be used effectively in the classroom (Orien, 1993).

Perhaps the most important aspect of a successful field activity is a clear articulation of the activities, goals, and expected outcomes of the field trip. The instructional goals of a field trip may be: 1) to catalyze, enrich or culminate instructional units, 2) to introduce a new unit of instruction to create interest in the subject or topic, 3) to present a main body of an instructional unit as a tool to enhance and motivate learning, or 4) to illustrate and reinforce facts, skills, and concepts as a follow-up for class work (paraphrased from Rudman, 1994). Whatever the motivation, field experiences should be integral to the overall course of study, rather than merely used as an enrichment or add-on activity (Orien and Hofstein, 1994).

A solid body of evidence indicates that the educational effectiveness of a field experience is strongly predicated on pre-field trip preparation (Falk et al., 1978). Orien and Hofstein (1994) have reported that the educational effectiveness is controlled by two major factors: the field trip quality and the "Novelty space" (or Familiarity Index). The quality of the field trip "is determined by its structure, learning materials, teaching method, and the ability to direct learning to a concrete interaction with the environment" (ibid). Novelty space is defined in terms of three variables: cognitive, psychological, and geographic familiarity. Students' ability to conduct higher cognitive tasks (e.g. problem-solving) is largely dependent on their familiarity with the field trip setting. Cognitive preparation may include hands-on activities working with materials, concepts, or skills needed to perform the tasks expected on the field trip; simulations that explain processes and phenomena; and review of students' prior knowledge about basic concepts relevant to the field trip. Psychological preparation should include descriptions of the length of the trip, a detailed itinerary of what to expect (including food and bathroom stops), time constraints for the field activities, expected weather conditions, detailed lists of clothing and supplies that will be needed, and in general, any other information that addresses the students' health, safety and security. Often students will have had little or no prior experience in the field, and uncertainty about what to expect will affect their performance. Geographic preparation might include locating field trip stops on a map, review of geologic maps and preparation of cross sections, or perhaps showing videos or a slide show of the field trip location(s). Students placed in a new physical environment spend a significant amount of time becoming acquainted with the new location before they engage the tasks at hand.

Rudman (1994) makes the following suggestions, that prior to a field trip leaders should:

1. Create goals and objectives which justify the purpose of the field trip.
2. Implement an introduction or orientation before the field trip departure (e.g., slide show, speaker, discussion on what to expect and how to behave).
3. Reduce the environmental novelty for yourself and the students. Make a pre-trip inspection yourself and learn how to use the (available) resources. If time, travel or expenses do not allow for this, phone calls or letters can be just as helpful.
4. Select a field trip site that provides hands-on, materials to manipulate. Trip leaders should stimulate interest through questioning, problem solving, exploration and investigation.
5. Allow students time to experience the excitement of exploration and discovery. Certain behaviors should be expected, but the field trip does not have to be a regimental, single file line of silent students.
6. Administer post-field trip materials, projects, or activities to help students reinforce and transfer the learning experience beyond the field trip.

Orien (1993) presents a model for the development and implementation of effective field trips:

1. The main instructional strategy of the field trip should be hands-on experience, concentrating on those activities that cannot be conducted in the classroom or laboratory.

2. A process-oriented approach should be used to achieve the objective of hands-on experience. This approach involves assignments that direct the students towards activities such as: observing, touching, identifying, measuring, and comparing. Follow-up activities of interpretation and drawing conclusions should be based on these basic processes.
3. Students should be prepared for the field trip. The more familiar they are with their assignment (cognitive preparation), with the area of the field trip (geographical preparation), and the kind of event in which they will participate (psychological preparation), the more productive the field trip will be for them.
4. The field trip should be used as an integration with a particular unit because concrete activities in the field provide a basis for meaningful learning.

To assess the effectiveness of the field trip experience, Orien and Hofstein (1994) used the following evaluative mechanisms:

1. Pre-field trip questionnaires were administered on students' background, attitudes towards field trips, attitudes towards geology and a pre-field trip achievement test was given.
2. During the field trip, direct observations were made of student performance, students were interviewed, and students' attitudes towards the field trip were collected via a questionnaire.
3. Post-field trip surveys and interviews were conducted to determine students' attitudes towards field trips and geology, and an achievement test was given.

It is necessary to have a basic understanding of students' prior knowledge, interests, attitudes, and pre- or misconceptions to help formulate the field trip activities. During the field trip it is also important to monitor student performance (what they can do and what they know) as well as interest and attitudes to ensure that the field trip is a positive and meaningful experience. Post-field trip activities are also important to help reinforce the lessons learned on the field trip, and to help students reflect on the relevance of the field experience to the rest of their coursework, and to their personal lives.

So how do these general recommendations translate to effective field trips in mineralogy and geology? Given constraints of limited time, resources, and geographic setting, field trips are special experiences in most curricula so extra effort should be directed towards making these positive and meaningful learning experiences for students. The overall quality of the field trip will depend on the structure of the activities, learning materials, and teaching methods:

- Factors such as the selection of the field area (Falk and Balling, 1980), the geologic setting, potential for collecting quality specimens at a sampling locality are all primary considerations. Decisions must be made about the relative merits of conducting a regional overview with many stops, or doing a focused activity at one (or a few) locations. Locke (1989) notes that during long road trips the travel itself is disconnected to learning, even when traveling through geologically interesting terrane. The goals of either a regional trip or a site-specific activity should be clearly articulated with well-defined outcomes of the field trip (e.g. road logs, descriptions of field sites, collections of representative samples, etc.).
- Preparation of technical materials is essential. This includes compilation of geologic maps and road logs, and it is increasingly common for field trip leaders to provide supplemental information such as photomicrographs, chemical variation diagrams, etc. of work previously done that would not otherwise be available in the field. Any equipment to be used must be fully functional and safe to use.
- Make sure that arrangements have been made ahead of time to ask permission to access private lands, and to inquire of private landowners and government officials the best routes for access to a given property. We have had a number of our local field sites closed by private landowners

because "rogue" field camps have trespassed on private lands without permission. Field sites may simply not be accessible due to local conditions such as weather, floods, landslides, or construction, and contingency plans should be in place.

- Instructional methods will vary greatly, and are largely dependent on the learning needs of the students. The goals, nature of assignments, expected outcomes, and assessment mechanisms must be clearly articulated for the students. Whenever possible, discovery and inquiry should be at the heart of the field trip exercises. Srogi and Baloché (this volume) describe a number of interactive learning strategies that apply equally well in the field as in the lab (see also Munn et al., 1995). Assign students various tasks to perform in preparation of a field trip -- let them gain some ownership and a sense of responsibility by doing literature searches, planning logistics, contacting property owners, etc. At beginning levels, it is probably better to engage "directed-discovery" or "guided inquiry" so that students will have a place to start their investigations, and a context to gain understanding. At more advanced levels, "open-discovery" becomes possible as students become confident in their ability to ask appropriate questions, seek evidence, and formulate interpretations. Different working groups should be encouraged to discuss and compare results. At the end of each activity, it is important to achieve closure through reflection of the key relationships that have been observed. Keep a reasonable schedule, and plan activities that have a high potential for success. Make sure all students feel welcome, valued, and engaged; make an effort to interact with all students, and at areas with limited exposure, make sure that all students have access to your explanations.
- Field trip activities should be carefully integrated with other course materials, as well as across the curriculum. Samples collected on a field trip can be used for further analysis in the laboratory to simulate, replicate or contribute to research already done in an area.
- Preparation of the students is essential for effective learning, as described above. In a mineralogy course, this should include pre-field trip exposure to the scientific content, principles, and methods that will be used on the field trip. Background material should be presented to give students the geographic and geologic context of the field trip.
- Students should be psychologically prepared to take the field trip. The health and safety of the students is of paramount importance (see Cummins, 1992). Don't forget to bring hard hats and safety glasses! Prepare for bad weather, insects, and the possibility of first aid emergencies (bee sting, snake bite, lightning strike, rock-throw, abrasions, poison ivy, heat stroke, twisted ankles, . . . , and worse). Provide advice for appropriate clothing and footwear. Make sure personal needs are accommodated including reasonable breaks for food and bathrooms. Be sensitive to the special needs of handicapped students, single mothers who have to be back on time because of child care, or working students who have to be back in time for the night shift. You will be guests at many facilities, and field experiences may be new to many students, so they will need advice on how to act and what to do.

Most professors of geology have had the great good fortune to do field work as an integral part of our professional careers. Many of us started careers in geology because we were attracted to field work. No matter what the geologic setting of our present work environment there is the possibility of sharing our field experiences with students. Our enthusiasm for field work should be contagious. And field trips provide a natural opportunity to employ the best practices of discovery-based learning. However, to optimize the effectiveness of the learning experience, we need to do more than say, "Let's load up the vans and go" (although there does remain an allure for many of us to be explorers of the great unknown). I believe that we generally do a good job preparing the technical aspects of a field trip -- amassing geologic maps, sample locations, organizing equipment. We must acknowledge the significant contributions made by individuals and professional societies who have compiled geologic road logs for our communal use. We must also recognize our responsibility to adequately prepare our students--cognitively, in geologic space and time, and psychologically -- to optimize the learning opportunities afforded by field trips.

Acknowledgment: Thanks to Peter Schade for helping to do the literature search on field trips and learning.

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EXERCISES WITH MINERAL NAMES, LITERATURE AND HISTORY

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INTRODUCTION

This is not primarily a laboratory exercise. It is a series of exercises I assign outside of class time, with the purpose of getting students to explore the literature resources that are available for mineralogy. The inspiration for the exercises comes from my exasperation with the repeated questions: “Why do we have to know so many minerals?” and “What about these minerals do we have to know?” Rather than saying “Everything that is important,” I hope to show students that what they need to know depends on what questions they hope to answer, and that mineralogy developed in historical context, parallel with other sciences.

The exercises are designed to stretch over several weeks. I begin the first exercise on the first day of class, and give one assignment per week, but the timing of assignments is flexible. Though the assignments can be incorporated, at the end, into a term paper or research report, I find the separate assignments to work better than the assignment of a single term paper at the outset. With the series of exercises, students do all of the work that might go into a term paper without the intimidating impression of a “magnum opus;” they do the work in a logical (?) progression of increasing complexity of information; the evaluation of students’ progress is incremental, so that timely help can be given; and the load of correcting the material is distributed over the term. If I assign a paper or report as the final product, I do not tell the students until they receive assignment 5. Specifically to avoid the impression that these are major assignments, I present them informally, just as handwritten notes that indicate the assignment and the due date.

ASSIGNMENT 1

Write a paragraph summarizing the origin and meaning of the mineral name you have been given. Provide references to where you found the information.

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I give each student the name of a mineral. These are taken from the short version of Deer, Howie and Zussman, and are specifically minerals that are not in their mineral sets in lab, and many of which are not in their course text. They are allowed to use any sources they wish to gather information on the mineral name.

When students hand in the mineral name exercises, I briefly discuss the types of literature resources that might be used, specifically pointing out the difference between primary and secondary sources. I also discuss the task of evaluating the reliability of sources.

There are three positive outcomes at this stage of the exercise.

1. Most students have gone to the library, and have accessed the library’s databases, looking for relatively uncommon mineral names. In some cases, they haven’t found anything.

2. They've begun talking to each other about how to do the exercise. The more inventive have started looking on the shelves in the mineralogy section, or in the reference section. Some have talked with librarians about internet sources and searches. The most exasperated have come to talk to me about how hard the assignment is.

3. Almost all students have had a taste of the "history" of mineralogy, and of how minerals are named. This can serve as a springboard for discussing ideas about what makes one mineral different from another, and what information is needed for distinguishing them.

ASSIGNMENT 2

Find three references in which your mineral is discussed. Hand in a sheet with these citations in GSA format, and a photocopy of the first page of each.

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After reviewing these assignments, I give "awards" (last year, "Looney Tunes" pens!) for the oldest citation (1909), the most recent citation (1996), the most bizarre citation (Journal of Neurophysiology!), the least useful citation (Grolier's Encyclopedia; National Geographic), the best overall assignment, the worst overall assignment, etc. The point is to involve as many students as possible, and to make the assignment series a light-hearted exercise. I reiterate the discussion of primary and secondary sources. I ask for photocopies because some students merely copy references from a catalog or index, and never look for the source material. If they do not look for a particular journal, they may never realize that some literature is not readily accessible, either because the library doesn't have the journal, or because the article is in a foreign language!

The outcome of this assignment is that students become aware of the range of literature that might need to be reviewed, and of the idea that each source has a unique format for reporting information. By now, some students start getting possessive about "their mineral."

ASSIGNMENT 3

Write a page-long summary of why your mineral is important. You can use the references you found in Assignment 2, but you might need to find more information.

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About halfway through this assignment, up to 30% of the students in the class have come to me asking "What do you mean by important? Do you mean that the mineral is used to make something, or what?" Depending on how vocal these students are, their questions can be used as a springboard for addressing the question of "importance" for the whole class. Many students will find the concept of importance to petrology unsatisfying ("Who cares whether it helps to determine the P-T-X conditions in Timbuktu?")! This offers the opportunity for developing the idea that the minerals students encounter in lab and class are but a fraction of those that are important to somebody, for something. Importance is in the eye of the mineral-holder. A student who was assigned melilite couldn't find references to melilite in terrestrial rocks, but found references to melilite in chondritic meteorites, and ended up concluding that melilite was important because it tells us how the solar system formed. Spodumene has been very successful, because recent work in the materials science and ceramics fields have capitalized on the spodumene structure, and several students discovered that there is mineralogy outside of geology. This assignment is the core of the discovery process that the series is designed to facilitate.

ASSIGNMENT 4

Interpret all of the information on the first page of the mineral's description in Deer, Howie and Zussman, and hand in an essay explaining all of the information.

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I give the students copies of the relevant pages from Deer, Howie and Zussman. Some of this is straightforward - the symbols for hardness, density, etc., should, by the fourth week of the term, be readily understood. But some of the data, particularly on unit cell size or optical properties, is opaque to the students. It encourages the students to teach themselves.

This assignment is geared to get students thinking about how they might identify the mineral. Many of them don't get the connection, because I don't babysit them through the exercise. They decide that optical properties or unit cell dimensions or strongest XRD lines are not important or relevant to them. These impressions might be corrected with the next assignment.

ASSIGNMENT 5

Identify this unknown, and write a report detailing your methods of identification.

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I give the students unknowns that contain their mineral, and support them in using whatever means they need to identify the mineral. I encourage them to use optical mineralogy as the initial identification method. For some minerals, it is virtually impossible to find appropriate samples (merwinite, anyone?), but for others, it is relatively easy. Most students haven't expected their mineral to show up as an unknown in their laboratory exercises because it is not in their mineral sets. I have followed through on this part of the assignment series only with a few students, simply for want of good samples. In no case were the students able to link their literature research with processing of an unknown. Some way, short of telling the students that "this unknown contains your mineral," is needed for making this linkage evident.

Obviously, the final report can be a full-blown term paper or research report, or it can be a one-page summary of the identification and analysis procedure.

The minerals I have used in this exercise to date are:

aenigmatite	allanite	astrophyllite	chloritoid	clintonite
eudialyte	kosmochlor	larnite	margarite	melilite
merwinite	mullite	piemontite	rankinite	spodumene
stilpnomelane	tilleyite			

I have found usable sample material for allanite, astrophyllite, chloritoid, eudialyte, margarite, melilite, piemontite, spodumene and stilpnomelane. Kosmochlor is a bust; I found it very difficult to get good information. I'm sure there are other and better minerals to use. My students do not have jadeite, pumpellyite, prehnite, glaucophane or lawsonite in their mineral sets, but do need to know about them in petrology; these would be obvious targets. I have restricted the exercise primarily to silicates because identification of many sulfates, phosphates and carbonates with optical methods is difficult. I have specifically excluded opaque minerals because I do not introduce my students to reflected light microscopy.

SHORT READINGS FROM THE AMERICAN MINERALOGIST: SNEAKY TOOLS FOR TEACHING SCIENTIFIC READING COMPREHENSION AND MINERALOGICAL CONCEPTS

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Overview

Writing across the curriculum has become an important concept, and even practice, in many schools. Reading across the curriculum is also important, but students already read a lot, don't they? Maybe, but what do they read? In mineralogy courses students usually read a textbook. Most textbooks are written to pass on information determined by generations past to generations present. This is fine for conveying general principles and information, and even some aspects of mineral science, but most mineralogy texts are really reference books that convey little about what mineralogists do, why they do it, or what minerals can tell us about the geologic environments in which they formed.

In 1988 I looked through recent issues of the *American Mineralogist* to find well-written, short articles that were clear, concise, that covered a narrowly focused topic, and that contained analytical data of some sort. For each article I wrote a 1-page sheet of questions and tasks for the students to answer for homework as they read the paper. The object of the questions and tasks was to help guide the students through the information and concepts in the paper.

The questions included simple things like the geographic location and the geologic environment of the samples. More sophisticated questions included such things as which curves on a graph corresponded to absorption by which atomic or molecular species in a mineral, or what experimental conditions favor dendritic vs. euhedral crystal growth. The answers to these questions were in part in the articles, in part in their textbook or class notes, and in part had to be determined by careful thought.

The tasks included plotting analytical data on graphs or doing simple algebraic calculations using data in the paper. The object was to look at the data in a slightly different way than was presented in the paper, to make certain points more clear and in some cases to allow interpretation beyond that in the paper.

When the homework is due I usually try to have some kind of discussion. The following method works well. Two students are told, days before the homework is due, that they will give a 10 minute presentation on the paper. I offer help preparing overheads and I help them plan the presentation. The other students are required to write two questions and to ask one of them during the discussion, to be answered by the class as a whole. These questions must be submitted to me in writing immediately prior to the discussion. I pay close attention to the submitted questions to see that they involved some thought. For example, "What color is the andalusite?" is not a question that required much thought if the abstract and the 2nd paragraph in the article gives the answer. "What color does andalusite usually have?" is a more interesting question that is not answered in the article but can be answered readily. Submission of written questions forces all students to participate in the discussion, to think a bit more about the article, and sometimes forces students to think about mineral science in general.

Although I have chosen these articles to be relatively short and simple, most students do not find them easy. They are shocked by how carefully they have to read the papers in order to understand the important points. This is quite different from reading a textbook, in which the information density is so low that a reader can often daydream through several paragraphs and not miss much. On the whole, however, students are rightly pleased with themselves after they have read and understood a real scientific paper. They have reported to me that they are glad to see what mineralogists and others are actually doing, and that the work is being done to answer fundamental questions about mineral chemistry and physics, physical properties, and the environments of mineral formation. By the end of the course, after having read four or five of these papers, I have noticed that students are more animated during discussions of mineral properties or chemistry than previous classes that never read such papers. I think students gain a deeper understanding of the nature and use of mineralogical research, and themselves become more confident in their understanding of mineralogy.

Using short, well-written articles to enhance teaching is easily adapted to other courses. I also use such articles in my Petrology course, although the articles happen to be from the journal *Geology* rather than from the *American Mineralogist*.

Special Reading: Instructions to Students (an Example)

Hazen and Sharp (1988): Compressibility of sodalite and scapolite. People generally think of solids as being incompressible, in contrast to gasses which are easily compressible. In reality, all materials are compressible to some extent. This paper describes compressibility measurements that were made on the two minerals sodalite and scapolite. As you read the paper, answer the following questions. For the graphs you may use graph paper or a spreadsheet.

- 1) What are the ideal chemical formulae of Ca-scapolite (meionite), Na-scapolite (marialite), and sodalite?
- 2) In what geologic environments is sodalite commonly found?
- 3) In what geologic environments is Ca-scapolite commonly found?
- 4) Plot on three graphs the following data from Tables 1 and 2 in the paper. Expand the scales on the graphs to clearly show the changes.
 - A) The sodalite a cell parameter $a(\text{\AA})$ vs. pressure P .
 - B) The scapolite a cell parameter $a(\text{\AA})$ vs. pressure P .
 - C) The scapolite c cell parameter $c(\text{\AA})$ vs. pressure P .

Put a straight line through the data points in each graph. These lines show how the minerals are compressed continuously along each crystallographic axis as the pressure is increased.

- 5) The changes in unit cell volumes of sodalite and scapolite with pressure are given in Tables 1 and 2 under the headings $V(\text{\AA}^3)$. Next to the cell volumes are columns labeled V/V_0 , which is the ratio of the cell volume at each pressure to the cell volume at 1 bar (0.001 kbar). This is a relative measure of how the volumes of the minerals change with pressure. On another graph plot the V/V_0 values for scapolite and sodalite. Put straight lines through the data.
- 6) Which mineral is more compressible, sodalite or scapolite? What is your evidence?
- 7) At 1 bar pressure the densities of sodalite and Ca-scapolite are 2.30 and 2.69 g/cm³, respectively. What are the densities of these two minerals at 26 kbar?

Annotated List of Articles Used

- Carlson, W.D., and Rossman, G.R. (1988) Vanadium and chromium-bearing andalusite: occurrence and optical-absorption spectroscopy. *American Mineralogist*, 73, 1366-1369. This is useful for teaching some principles of optical absorption, color, and pleochroism in minerals, and it is a good example of the utility of the crystal chemical rules of ionic solids for deciding which site or sites different ions might occupy.
- Hazen, R.M., and Sharp, Z.D. (1988) Compressibility of sodalite and scapolite. *American Mineralogist*, 73, 1120-1122. An excellent, short paper showing that solids are compressible, and that mineral volumes and densities must change as the pressure varies.
- Jambor, J.L., Bladh, K.W., Ercit, T.S., Grice, J.D., and Grew, E.S. (1988) New Mineral Names: Atlasovite. *American Mineralogist*, 73, 927. This is a brief abstract presenting a new mineral, including its chemical composition, ideal formula, and various physical, chemical, and structural properties. I have found it useful to give this to students to look at on the first day of class (they are usually horrified), and then again in the last week of class as an exercise to explain different parts of the abstract. By that time they are usually quite familiar with most of the concepts in the abstract. It helps show them how much they have learned.
- Murrowchick, J.B., and Barnes, H.L. (1987) Effects of temperature and degree of supersaturation on pyrite morphology. *American Mineralogist*, 72, 1241-1250. This paper helps show students that one mineral may look different depending on the conditions of growth. The experimental apparatus is described in words, and I have the students make a sketch of the apparatus based on the description. This is a long article, but about 1/3 of it is SEM photos.
- Norimoto, N. (1989) Nomenclature of pyroxenes. *American Mineralogist*, 73, 1123-1133. This is a long, advanced, but excellent paper that dwells on the crystal chemistry of pyroxenes. It is useful toward the end of the course after students have become reasonably comfortable with crystal chemical concepts.
- Parnell, John (1988) Native platinum in pyrobitumen from Fonda, New York. *American Mineralogist*, 73, 1170-1171. This odd occurrence of platinum is near Union College, so it interests the students in that respect. It also ties the mineral occurrence to regional geology and tectonics, since we can discuss the tectonic history of eastern New York State and speculate on the timing of migration and trapping of the hydrocarbons and platinum.
- Rosenberg, P.E. (1987) Synthesis of metastable Ca-Mg carbonates. *American Mineralogist*, 72, 1239-1240. This paper describes the experimental synthesis of a variety of Ca-Mg carbonate materials intermediate in composition between end member calcite and dolomite. The data are somewhat 'fuzzy', and require some interpretation to conclude that there are indeed four synthesized phases rather than just a continuum. The students have to plot the analytical data to see if the author's conclusions are reasonable.
- Solomon, G.C., and Rossman, G.R. (1988) NH_4^+ in pegmatitic feldspars from the southern Black Hills, South Dakota. *American Mineralogist*, 73, 818-821. This paper illustrates the use of non-visible light spectroscopy for understanding the crystal chemistry of minerals. Students have to match absorption peaks on a graph with proposed absorbing species, and they have to explain why this pegmatite contains ammonium-bearing feldspar whereas mineralogically similar pegmatites nearby do not.

WONDERING, WANDERING, AND WINNOWING: THE WWW AND MINERALOGY

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Revisions to this document (as available) will be found at:
<http://www.geology.wisc.edu/class/g360/wwwlab.htm>

Students: Clicking on my email address above will open an email window into which you can type the answers to the questions asked below. If you are not at the University of Wisconsin-Madison PLEASE change the email address in your email document to that of your professor or TA.

[1] Basic World Wide Web Searching

This first exercise will be old news to many of you but possibly the first time for others. If you are an experienced WWW user, help someone else in the class get started.

Locate and start up the WWW browser on your computer. In most cases this will be some version of Netscape and I will assume from here out that you are, in fact, using Netscape. Other browsers will work as well but the location of buttons and menus will probably differ. I designed this lab using Netscape 2.02 for the Macintosh, it works fine with Netscape 3 and I have checked most of it on a Windows 95 machine running Netscape 3 as well.

Click the 'Net Search' button (or choose Internet Search from the Directory menu) and you will be presented with a field in which you can type search terms, a choice of subjects or categories with which to limit the search, and a choice of search "engines" such as Yahoo, Lycos, Alta Vista or Magellan. To begin, choose Yahoo and click on the hot linked text 'Education'. On the subsequent screen, type "mineralogy" into the input field and then either click the 'Search' button or hit the 'Return' or 'Enter' key on the keyboard - all three actions should have the same effect of submitting your search to the chosen search engine.

When the search returns its results, spend a few minutes following the links that were located. Unless things have changed dramatically since I did this, the number of links returned by the search are few indeed. **Why do you think this is? How would you submit a site so that Yahoo can find it?**

What happens if you follow the Yahoo links 'Science' and then 'Earth Sciences' and then search for "mineralogy"?

Backtrack and then repeat the search for the term "mineralogy" using the Lycos search.

How many hits did you get this time?

Now that we have wondered, let's wander and winnow. Each class member should spend 10 minutes assessing a different set of 10 hits returned by the search. Let's arbitrarily number the students and have student 1 take hits 1-10, student 2 takes 11-20, and so on. **What is the best site you found? Make a list of these. How many are truly relevant to this course?**

[2] Major Mineralogy/Geology Sites

Now lets see what the results of many hours of searches like those you just completed could turn up - lets visit some of the most helpful home pages for our subject.

Open up a connection to John Butler's site at the University of Houston:

<http://www.uh.edu/~jbutler/anon/anonfieldtrips.html>

This link has opened several pages below the University of Houston's home page and provides a great place to start our tour. Clicking on the 'Courses by Title' hot text lets you choose Mineralogy and then be presented with 19 choices from around the world.

Choose the Iowa State link to Ken Windom's Mineralogy course:

http://www.public.iastate.edu/~geology_311/homepage.html

Ken's course home page provides links to several national and international organizations and agencies. Choose the 'Computer-based Assignments' text and then click on Exercise 3. This simple exercise highlights some of the information readily available from the links provided. **Work through at least 3 of the questions that Ken asks here.** (A caveat: when you do this exercise now, you may well run into some dead ends which presumably weren't there in the fall of 1995 when Ken made this page. For example the link to the Canadian Mineralogist is now <http://www.umanitoba.ca/geoscience/mac/> instead of what is on Ken's page. This is a general lesson in using the WWW for education. Lecture notes can't afford to be static; instructors must continually change and update links.)

Now try the University of Colorado Mineralogy link.

<http://xtl5.colorado.edu/~smyth/syl3010.html>

This syllabus has several lectures available which cover the first couple of weeks of a typical course. You may want to return to this material for an alternative explanation (to that given by your professor) of the arcane subjects of point groups and the like.

Colorado also offers a course in Crystallography and Crystal Chemistry which is aimed at students either one or two years after Mineralogy. Only the syllabus is provided here.

Mickey Gunter at the University of Idaho provides a very rich set of resources for his Mineralogy course which he taught during the Spring 1997.

<http://www.uidaho.edu/~mgunter/geol249/geol249.html>

In addition to the lecture notes and handouts, he provides old tests, lab exercises, links to the rest of the world, and links to local Idaho mineral collecting. It is this last that sets this site apart and provides the student with the "value added" which makes the WWW useful and exciting.

Jack Rice at the University of Oregon clogs up the beginning of his otherwise excellent course home page with a LARGE interlaced GIF file which, while beautiful, is painfully slow to download over a modem or during the busy times of the day.

http://darkwing.uoregon.edu/~jrice/geol_311/geol_311.html

His lecture notes are comprehensive for this apparently 10 week course (quarter system?) and all that is lacking are the silicates which must be covered in the next quarter.

And last but certainly not least ;-) are links to two courses at the Univ. of Wisconsin.

<http://www.geology.wisc.edu/~jill/geo306.html>
<http://www.geology.wisc.edu/class/g360>

The much more polished course is Jill Banfield's Gems course Geology 306 for which she and I received internal UW funding to help develop a WWW course that could theoretically be taken much like a traditional correspondence course. (Jill was on leave during the 96-97 academic year and in fact taught this course from Japan.) Our Mineralogy course is a team taught effort and a visit to last year's web page shows it to be about 3/4 baked. I will be updating and extending the web presence of this course in the future.

These courses share some very rich resources which again point out the utility of the WWW for content delivery. On the Mineralogy Menu page click on the Crystal Structure Movies hot text. These movies were made with CrystalMaker 1.1.4 and were designed to show specific parts or aspects of each minerals structure. We use these in lecture (using a projection system) and generally talk about these structures as we step through the movie's frames.

The Gems course has quite a number of animations of geological processes leading to the formation of specific minerals and optical effects in gem stones. **What are some major differences between the formation conditions of agates and tourmaline?** See in particular:

<http://www.geology.wisc.edu/~jill/Lect3.html>

[3] Basic Resources

There are lots of basic science resources being maintained at web sites around the world. Below are some of these with comments.

Periodic Tables:

A very comprehensive periodic table site is the WebElements page which originated at the University of Sheffield in England but is mirrored at more than a dozen sites; you will want to use one that gives you maximum performance. Most of the sites have version 1.2.1 while the Sheffield site has a late beta version 2 which takes advantage of frames and has much more information. The response time may well depend on the time of day, the day of the week, and quite possibly the phase of the moon. The Berkeley site, which used to be much faster than the one at Boston College, now defaults to the Sheffield site; try the Illinois site; your mileage may vary.

University of Sheffield: <http://www.shef.ac.uk/~chem/web-elements/>

UC Berkeley: <http://www.cchem.berkeley.edu/Table/index.html>

University of Illinois: <http://bmrl.med.uiuc.edu:8080/periodic/>

Boston College: <http://chemserv.bc.edu/web-elements/web-elements-home.html>

Another very nice periodic table can be found at Los Alamos National Labs:

<http://mwanal.lanl.gov/CST/imagemap/periodic/periodic.html>

Table of Nuclides:

Berkeley National Labs maintains a mirror to a site created in Korea. This may be overkill for introductory mineralogy but keep this for a future geology course.

<http://datwww.dne.bnl.gov/CoN/index.html>

(this site is also known as)

<http://necs01.dne.bnl.gov/CoN/index.html>

Atomic Radii:

A very nice compendium of data on this subject. **Compare the data on important rock forming elements with the data published inside the covers (or possibly in an appendix) of your text book. What are the largest differences? How can both of these compilations be right?**

<http://www.iumsc.indiana.edu/helps/radii.html>

Alphabetical Mineral Reference:

The following on-line glossary of mineral names provides basic occurrence information for MANY common and not so common minerals. **What anionic groups are found in the minerals carnotite and purpurite?**

<http://www.geology.wisc.edu/~jill/glossary2.html>

Mineral Databases:

The ATHENA site also has a very detailed mineralogy database program which is searchable by name, variety, and composition. **Are there more Bromides or Iodides found as minerals? (I would suggest using the Mineral Search function rather than trying to count them from the Halides listing.)**

<http://un2sg1.unige.ch/www/athena/mineral/mineral.html>

The Mineral Gallery is a commercial operation but they sure have a bunch of nice pictures and quite a lot of information about each of their specimens.

http://mineral.galleries.com/minerals/by_name.htm

Thermodynamic Calculations:

This site at the University of Calgary can be used to perform geothermobarometry calculations directly on the WWW. It is probably more useful for Petrology classes. **Where does the triple point of SiO₂ for the minerals alpha quartz/beta quartz/coesite occur in P-T space? How does the result agree with the plot in your text book?**

<http://ichor.geo.ucalgary.ca/~tmg/Webinveq/rgb95.html>

[4] Lists of Links

There are lists of links EVERYWHERE on the web - many are only a few items long while others are very comprehensive. I have only mentioned 4 here.

[1] A HUGE resource is that maintained by Phillip Ingram at Macquarie University in Sydney, Australia. A monthly updated FAQ (Frequently Asked Questions) document can be gotten by one of the following two non-WWW mechanisms:

i) send mail to: mail-server@rtfm.mit.edu with the following line in the body of the message -

send_usenet/news.answers/geology-faq/geosci-resources/part1

ii) by anonymous ftp to:

[rtfm.mit.edu/pub/usenet/news.answers/geology-faq/geosci-resources/part1](ftp://rtfm.mit.edu/pub/usenet/news.answers/geology-faq/geosci-resources/part1)

Even more info is available on the 2 WWW pages he maintains at:

The Virtual Earth: http://atlas.es.mq.edu.au/users/pingram/v_earth.html

The Soft Earth: http://atlas.es.mq.edu.au/users/pingram/s_earth.html

[2] The University of Calgary maintains a Virtual Library of Earth Science Resources:

<http://www.geo.ucalgary.ca/VL-EarthSciences.html>

[3] There is a huge list of resources to be found at the ATHENA site in Geneva, Switz.

<http://un2sg1.unige.ch/www/athena/mineral/mineral.html>

[4] Andrea Koziol at the Univ. of Dayton has a new list of links which she updates with some regularity:

<http://www.udayton.edu/~geology/resminpet.html>

[5] Optics and Mineralogy

A somewhat brief but polished treatment of optics and minerals is given by Charlotte Gladstone at the University of Bristol in England. This page also provides additional links for more in depth study.

<http://www.bris.ac.uk/Depts/Geol/opmin/mins.html>

Check out the Petrographic Workshop at UCLA. Many minerals are represented and thin section photomicrographs (as jpg images) and basic optical properties are given. This is a major resource. **How would you describe the twinning seen in the mineral microcline as observed in thin section?**

http://pong.igpp.ucla.edu/pet/pet_intro.html

Mickey Gunter has the beginnings of an optics page at:

http://www.uidaho.edu/~mgunter/opt_min/opt_min.html

Gary Byerly at Louisiana State Univ. has a home page for the optics course that he teaches. This is really only an outline of the course and while it is probably useful for his students, it doesn't provide much value for the outside surfer.

<http://gbyerly.geol.lsu.edu/geology/optics.html>

[6] Crystallography

There is LOTS of information on crystallography available on the WWW but a few searches will convince you that most crystallography is done by chemists, engineers, and biologists interested in inorganic and organic substances having nothing to do with geology. Two links which are useful are given below:

Crystallography World-Wide is mirrored around the world - the original reference URL is:

<http://www.iucr.ac.uk/cww-top/crystal.index.html>
Try the San Diego Site: <http://www.sdsc.edu/Xtal/vl/>

The structures at this next site are VRML and .zip files which need to be viewed on a PC (not Macintosh) computer with a dedicated viewer.

http://tutor.oc.chemie.th-darmstadt.de/Poly/VRML/silicat_e.html

[7] Pretty Pictures

Mineral Gallery

<http://mineral.galleries.com/>

Gems and Gemology

<http://www.geology.wisc.edu/~jill/geo306.html>

Smithsonian Gem and Mineral Collection

<http://galaxy.einet.net/images/gems/gems-icons.html>

Suggestions to Instructors

The purpose of this laboratory exercise is to introduce the student to Earth Science resources on the World Wide Web (WWW) and in particular provide access to material which can be useful throughout a typical Mineralogy course. One way to use this lab would be during the first week of classes (typically immediately after Labor Day at Wisconsin) prior to having covered enough material in lecture to have a "real" lab. If you don't have access to a computer lab so that all the students in a lab section can work on this at once (singly or in pairs) or if you have some other favorite first lab, one could introduce this exercise and plan to have the students do much of this on their own.

My students using most browsers can click my email address at the top of the exercise and a 'mailto' window will open into which they can type the answers to the questions. When they are done they can email their results to me directly. If you encourage your students to do these exercises and submit the results to you PLEASE MAKE SURE THAT THEY REPLACE MY EMAIL ADDRESS WITH YOURS!

All the WWW URL references are complete paths therefore if you wish to copy the source for this document and put it on your own computers to speed interaction, the links should survive intact. I plan to maintain and update the original on a regular basis.

Submit corrections and suggestions for additions to me. During the testing phase the one comment that I heard several times was that the WWW would be more useful and helpful if specific questions/problems were keyed to individual lectures or subjects. In other words, tailor made weekly exercises should follow from this overview. If you write up such exercises and are willing to share them, I will link them to this page as appropriate.

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CRYSTAL GROWTH – FAST AND SLOW

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Background

Mineral shapes and sizes are spectacularly diverse, and the means by which depositional environments control crystal morphologies remains an exciting area of research. Some minerals never achieve crystal sizes beyond a micron (e.g., kaolinite, many Mn oxides), whereas others can grow as single crystals that weigh several tons and extend many meters from tip to toe (e.g., quartz, feldspar). Likewise, some minerals nearly always exhibit the same habit (e.g., the micas), while 300 different forms have been described for calcite alone.

Most minerals show some variability in the habits they adopt, though sometimes the forms that have developed are hard to discern in natural rocks. In many slow-cooling igneous melts, for example, emergent nuclei crowd each other to the point that no single crystal can evolve a euhedral morphology; in the resulting cumulate textures, minerals are space-filling and can exhibit curvaceous boundaries. Even when parent rocks contain minerals with fully formed faces, erosive processes can erase the original morphology as minerals are recast in sedimentary deposits.

Fortunately for the highly tuned esthetic sense of every mineralogist, many minerals do manage to attain ideal forms. Euhedral crystals are particularly common within rock cavities that have been flushed with supersaturated solutions or vapors. Geodes containing large, prismatic quartz crystals are a well-known example. Similarly, well-developed faces characterize phenocrysts that grow slowly within volcanic magma chambers. The high-temperature annealing that accompanies regional metamorphism can lead to the formation of distinct faces on pre-existing minerals, and the cementation that follows the percolation of fluids through sedimentary rocks can sharpen the boundaries of quartz and calcite grains.

An enormous number of variables will constrain the shape of a growing crystal. Important factors include:

- 1) the temperature and pressure profile of the system;
- 2) the chemistry and structure of the mother phase (vapor, solution, or melt);
- 3) chemical and heat transport properties of the crystal and the mother phase;
- 4) the lattice symmetry of the crystal;
- 5) the surface structure of a given {hkl} face; and
- 6) the presence of defects on the growing face.

Transport characteristics of the crystal and the solution are in turn influenced by the density, viscosity, and flow velocity of the parent solution, the growth rate of the crystal face, the area of the solid-solution interface, and the thickness of the boundary layer.

For this laboratory, we will observe directly the role that the rate of crystallization plays in directing crystal shape. If we could perform this laboratory over geological time scales, we might attempt to duplicate the precipitation of common silicates from low-temperature fluids, as occurs in sedimentary environments. But we have only three hours, so we will work with materials that emulate natural crystal growth processes. In the first set of experiments, we will mix solutions from which euhedral crystals grow over one to two weeks. For the second set of experiments, we will observe disequilibrium crystallization over time scales of seconds.

Warnings

- 1) Some of the chemicals used in the slow and fast growth experiments are toxic. Despite their pretty colors, none should be eaten, and hands should be washed following the lab. Likewise, tetrahydrofuran (THF) is an ether and should only be used in well-ventilated areas away from flames or high heat.
- 2) Liquid nitrogen can cause frostbite. Care should be taken to prevent splashing when pouring.

Slow Growth Experiments

Materials for each team of 2 to 3 people:

400-ml beaker
Water (distilled if you have it)
Stirring rod
Weighing paper
Balance
Hot Plate
Thread
Kimwipe & Rubberband

Compounds (Do not eat):

- | | |
|--|--|
| 1) NaCl
Sodium chloride
Halite | 5) $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$
Potassium sodium tartrate hydrate
Rochelle salt |
| 2) $\text{K}_3\text{Fe}(\text{CN})_6$
Potassium ferricyanide
Red prussiate of potash | 6) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
Sucrose
Table sugar |
| 3) NaNO_3
Sodium nitrate
Nitrinite | 7) $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
Alum |
| 4) $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
Cupric acetate monohydrate | |

General Procedure

You will create supersaturated solutions by adding the powdered compounds to water in ratios specified below. The solutions will be heated and stirred until the solids have dissolved, and then the liquids will be allowed to cool to room temperature. If seed crystals are available, they can be secured by a thread in a slip knot and suspended in the solution from a stirring rod or pencil lying across the mouth of the beaker. A kimwipe should be placed over the top of the beaker and fastened with a rubber band to keep out dust. Solutions will be monitored over the next two weeks for crystal growth during solvent evaporation.

<u>Compound</u>	<u>Add to 200 cc H₂O</u>
1) NaCl	100 gm
Halite	
2) K ₃ Fe(CN) ₆	93 gm
Potassium ferricyanide	
3) NaNO ₃	110 gm
Sodium nitrate	
4) Cu(CH ₃ COO) ₂ · H ₂ O.....	20 gm
Cupric acetate	
5) KNaC ₄ H ₄ O ₆ · 4H ₂ O.....	260 gm
Rochelle salt	
6) C ₁₂ H ₂₂ O ₁₁	460 gm
Sucrose	
7) KAl(SO ₄) ₂ · 12H ₂ O.....	40 gm
Alum	

Questions -- Slow Growth Experiments

- 1) Many cubic materials (such as halite and galena) precipitate as cubic crystals, with {100} as the dominant family of faces. The vectors from the center of the cube to the 8 apices of the cube are normal to the {111} faces. What does this observation suggest about the growth rates of the {100} faces in comparison with the growth rates of the {111} faces? In general, do the best developed faces of a crystal grow more rapidly or less rapidly than the other faces? (Hint: The correct answer is counter-intuitive for most people.)
- 2) What are hopper crystals? Based on your answers to Question 1, how might you explain the development of these peculiar crystal morphologies?
- 3) Despite the complexity of the crystal growth process, a simple rule formulated by Auguste Bravais in 1860 successfully predicts crystal shapes based only on the translational lattice symmetry of the structure. A modern statement of that law (Zoltai and Stout, 1984) is as follows: *The rate at which a crystal face {hkl} grows is inversely proportional to the interplanar spacing d_{hkl} corresponding to that face.*

Does the prominence of the {100} family of faces for many cubic materials obey this law? Why or why not?

4) Based on Bravais's law, what is the most prominent face expected for:

- a) Galena (cubic: $a = 5.94 \text{ \AA}$)
- b) Almandine (cubic: $a = 11.53 \text{ \AA}$)
- c) Muscovite (monoclinic: $a = 5.19 \text{ \AA}$, $b = 9.04 \text{ \AA}$, $c = 20.08$, $\beta = 95.5^\circ$)?
- d) Zircon (tetragonal: $a = 6.60 \text{ \AA}$, $c = 5.98 \text{ \AA}$)?
- e) Quartz (hexagonal: $a = 4.91 \text{ \AA}$, $c = 5.41 \text{ \AA}$)?

According to Klein and Hurlbut, which faces are commonly observed in natural crystals of these minerals? Does Bravais's law successfully predict the shapes for all crystals?

- 5) Bravais's law may be rationalized in the following manner: The growth of a given crystal face is accomplished by the addition of individual unit cells to that face. The larger the area of attachment of a single unit cell, the stronger that attachment will be. The stronger the attachment, the faster the growth of that face.

All primitive unit cells for a given lattice must have the same volume. If A_{hkl} represents the area of an hkl face for a primitive cell, and d_{hkl} represents the interplanar hkl spacing, what is the volume for that unit cell?

Does d_{hkl} vary directly or inversely with A_{hkl} ?

By this logic, can you explain the basis for Bravais's law?

- 6) The equilibrium crystal shape for a mineral obeys the point group symmetry that characterizes the mineral. The space group symmetries for the crystals grown in these experiments are as follows:

<u>Compound</u>	<u>Space Group</u>
Halite	$Fm\bar{3}m$
Potassium Ferricyanide	$P2_1/c$
Sodium Nitrate	$R\bar{3}c$
Cupric Acetate	$A2/a$
Rochelle Salt	$P2_12_12$
Sucrose	$P2_1$

What are the crystal classes associated with these space groups (see Table 3.5 in Klein and Hurlbut)? Using this information, list the sets of ideal forms that might be expected for each compound.

- 7) One theory that attempts to incorporate the effects of atomic structure in crystal growth processes is called the periodic bond chain (PBC) theory. Many materials contain chains of atoms that are linked by strong chemical bonds. Silicates typically contain these chains as networks of silica tetrahedra. When atoms attach to a growing crystal so as to extend the chain, the attachment is strong and the growth in that direction is fast.

What is the expected morphology for a crystal built of linear tetrahedral chains aligned parallel to c ? What are the typical habits of pyroxene and amphibole? Based on PBC theory, what is the expected shape of quartz crystals? How can PBC theory be used to explain the platy habit of mica?

Fast-Growth Experiments

Materials: Binocular microscope
(For each person) Petri dish (5 cm diameter)
2 glass microscope slides (3" x 1")
2 cover slips (24 x 40 mm)
2 medium (No. 50 or No. 20) binder clips
Pipette
2 2" x 2" sheets polarizing film (size is not critical)
Styrofoam cup

Chemicals: Tetrahydrofuran (THF)
Liquid Nitrogen
Copper Chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (optional)
Methanol (optional)

General Procedure

A stock solution for these experiments is prepared by mixing pure THF with water in a ratio of 1.5 : 1 by volume. Once this THF solution is mixed, 2 or 3 drops should be placed in the center of a microscope slide. A glass cover slip is then placed at each end of the slide. The cover slips should not touch or interfere with the THF solution; they serve merely as spacers. The second glass slide is placed over this assemblage and is clamped into place with a binder clip at each end of the sandwich. Ideally, the THF solution forms a thin film in the center of the assemblage.

A petri dish is placed under the binocular scope, and liquid nitrogen is poured from a styrofoam cup into the petri dish. The THF assemblage then is placed above the boiling nitrogen on the petri dish. The student should focus the binocular scope on the solution and observe the crystallization of the THF.

(Optional for those with no hope of obtaining liquid nitrogen) A cupric chloride solution can be made by scooping a few grams of CuCl_2 into 100 ml of methanol (exact amounts are not important). A few drops of this solution may be placed on a glass slide, and rapid crystal growth may be observed by binocular or petrographic microscopes as the alcohol solution evaporates.

Questions -- Fast Growth Experiments

- 1) Once crystallization begins, do the crystals grow rapidly or slowly? Do the crystals advance haltingly, or at a constant velocity, or does velocity increase as the crystals grow larger?
- 2) At equilibrium conditions, this THF solution crystallizes at 2°C . The temperature of boiling liquid nitrogen is 77 K. Do you think that crystals start to form exactly when your solution reaches 2°C or when the temperature is considerably lower? Why might a solution require a large degree of undercooling to initiate crystal growth? Do you suppose that the reverse process of melting requires a similar degree of overheating before liquid appears? Why not?

- 3) Draw the textures produced by your crystallized solution of THF. These crystal shapes are called dendrites, based on their branching morphology (the Greek root means tree-like). In what natural settings have you observed dendritic crystals?
 - 4) Dendritic crystallization can occur when a very steep temperature gradient exists across the crystal-solution interface. In other words, the temperature of the solution decreases rapidly away from the crystal face. A steep gradient is typical of strongly undercooled disequilibrium conditions. If a crystalline protrusion appears on an otherwise smooth crystal face, why might a steeply dipping temperature gradient promote the growth of that bump?
 - 5) Will the tendency for a material to crystallize with dendritic morphologies increase or decrease with:
 - a) Steeper temperature gradients between the solid and the liquid?
 - b) Higher latent heats of crystallization (the heat energy produced by the process of solidification)?
 - c) Higher thermal diffusivities for the solid and the liquid (i.e., the ability of the solid and liquid to transport latent heat away)?
 - d) Higher heat capacities for the solid and liquid?
 - e) Increasing impurity concentration at the solid-liquid interface?
 - 6) Place the frozen THF assemblage between cross-polarized films. Does any light pass through the crystals? What does this tell you about the symmetry of the crystals? These structures are called clathrates, which are structurally similar to zeolite. At the bottom of the ocean, clathrate structures that consist of an H₂O framework encaging methane molecules are quite common.
 - 7) Allow the THF crystals to melt. Disassemble the slides. Wipe off the THF solution, and place 2 to 3 drops of pure water on the slide. Reassemble as before and place over liquid nitrogen. How does the crystallization of ice-I differ from that of the THF clathrate?
 - 8) Place the frozen water between crossed polarizing film. Does light shine through? What does this result tell you about the symmetry of ice-I? Is the structure of ice-I the same as the structure of THF clathrate?
- (Optional for those working with cupric chloride)
- 9) What is the shape of the crystals that form upon evaporation of the solvent? Are individual crystals isolated, or do they occur as clusters? What is the geometric shape of the clusters?
 - 10) Acicular (needle-like) crystal growth is strongly analogous to dendritic growth. Filamentous THF crystals grow from solutions undercooled using liquid nitrogen, and the THF solutions are characterized by strong temperature gradients due to the proximity of liquid nitrogen. Acicular CuCl₂ crystals grow from evaporating solutions at constant temperature, but disequilibrium of another sort promotes fibrous crystal growth. What kind of gradient develops around an emerging crystal in an evaporating solution? Does the gradient become steeper or more shallow with increased evaporation of the solvent? Why might the growth of a protuberance on a smooth crystal face be accelerated under these conditions? Using these ideas, can you provide a general explanation for acicular growth from an evaporating solution?

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where T_M is the melting temperature, T_∞ is the temperature of the fluid at an infinite distance from the crystal surface, L is the latent heat, and c is the specific heat of the fluid. Higher latent heats will raise the temperature of the fluid at the interface and thus decrease the amount of undercooling. However, latent heat must be normalized by c , the degree to which the temperature of the fluid will increase in response to the heat absorbed. The higher the heat capacity, the smaller the change in temperature for a given latent heat, and the more likely that a steep temperature gradient will be maintained. Similarly, steep temperature gradients are difficult to maintain when thermal diffusivities are high. The presence of impurities often serves to lower thermal diffusivities by acting as an energy sink or barrier, and thus impurities can help maintain a disequilibrium thermal profile near the surface.

In summary, the tendency for dendritic crystallization:

- a) Increases with steeper temperature gradients;
 - b) Decreases with higher latent heats;
 - c) Decreases with higher thermal diffusivities;
 - d) Increases with higher heat capacities;
 - e) Increases with higher impurity contents.
- 6) The THF clathrate hydrates are cubic and isotropic, and no light passes through cross polars.
 - 7) Although H_2O obviously can form beautiful dendrites in snowflakes and rime frost, in my experience the crystallization of ice in this experiment produces a cumulate texture.
 - 8) As ice-I is isostructural with tridymite, its symmetry is hexagonal and its optical character anisotropic. Birefringent colors should be apparent in cross-polarized light.
 - 9) Cupric chloride crystals typically grow as acicular crystals within spherulitic clusters. In contrast to the dendrites observed with THF clathrate hydrates, these cupric chloride crystals rarely exhibit secondary and higher level branching.
 - 10) Whereas undercooling can lead to steep thermal gradients near the crystal-liquid interface, evaporation can lead to solutions that are extremely supersaturated, and steep compositional gradients develop near the interface. Adsorption on the crystal surface leads to a local depletion of solute, but concentrations rise sharply with greater distance from the surface. A small protuberance will come in contact with solute-rich regions and continue its growth, setting up a positive feedback dynamic that is analogous to dendritic growth in undercooled conditions.

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GROWING CRYSTALS ON A MICROSCOPE STAGE

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Introduction

Many compounds crystallize rapidly from evaporating solutions, and many can be crystallized from melts. Because of this, it is possible to do simple crystallization experiments and to watch crystals grow over short times. Students can study several different compounds during one lab period. Crystal habit, growth zones, nucleation, deformation textures--students can examine many things quickly and easily. During the past year, we have studied many different compounds, and tried various techniques, as we worked to develop new exercises for our mineralogy students. We have found the results to be fun and exciting, and we summarize some of them here. These are preliminary results only, but we think some great laboratory projects can be developed using the approach we describe. We have spent six months precipitating crystals from various aqueous solutions, but have only just begun growing them from melts.

Equipment

The experiments require only minimal equipment: a hot plate with a calibrated temperature scale (or a thermometer for measuring hot plate temperature), a "dimple" plate (depressive slide plate), and a petrographic microscope. Additionally, vials, pipets, mortar and pestle and other standard lab equipment are needed.

Compounds Studied

We obtained simple and intriguing results by precipitating crystals from saturated solutions of kernite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$), sylvite (KCl), halite (NaCl), smithsonite (ZnCO_3), rhodochrosite (MnCO_3), gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) and an unnamed organic compound $\text{CaH}_4(\text{C}_3\text{S}_3\text{N}_3)_2 \cdot 11\text{H}_2\text{O}$. Additionally we grew crystals from molten para-dichlorobenzene, octachloropropane, biphenyl, thymol, and camphor. (We are indebted to W. D. Means for suggesting these compounds and providing materials; see Means, 1986).

Procedure

For precipitation experiments, we prepared solutions by finely grinding minerals, putting about 0.5 gm of the resulting powder and some warm water in a one dram vial, and shaking. Kernite, sylvite and halite readily dissolve, but the carbonates do not. To help dissolution, we added HCl to some carbonate solutions. We also prepared one solution by combining equal amounts of saturated kernite and sylvite solutions. Once a presumed saturated solution was prepared, we placed a drop or two in a dimple on the dimple plate, and then heated it on the hotplate. Periodically, we removed the dimple plate from the hotplate and examined it under a petrographic microscope; when crystallization began, we left it on the microscope stage. For the crystallization experiments, we melted crystals between two glass slides and allowed them to recrystallize (Means, 1986).

Selected Results

halides: Sylvite and halite are particularly intriguing because as crystals begin to form they develop pronounced growth zones. We added food coloring to the solutions to make the zones more pronounced. Forms included dodecahedrons and cubes. Growth is from the outer parts of a dimple toward the center, and is quite rapid if the dimple plate is very hot. Microstructures and other imperfections are readily apparent if crystallization is fast. We were not able to obtain euhedral crystals from commercial ionized salt, presumably because it is processed to reduce recrystallization.

kernite: Kernite crystallizes typically as fine needles, sometimes forming radiating splays. Rare monoclinic plates may form. Needles propagate through the solution and striations appear on the larger crystal faces, but growth zones are not obvious. Crystallization is quite rapid; in fact, it is so rapid that if the dimple plate is too hot it occurs practically instantaneously.

sylvite and kernite together: As the solution evaporated, kernite needles grew. When the last crystals of kernite formed the sylvite crystals began to appear. Sylvite soon completely covered the kernite needles, which generally settled to the bottom of the dimple. Getting the two to crystallize simultaneously, or nearly so, might be possible, using a different composition solution.

smithsonite: We had difficulty precipitating ZnCO_3 because of its low solubility. Addition of HCl increased solubility and small well-formed crystals with rhombohedral and scalenohedral forms developed on evaporation, but they were crystals of zinc chloride, not zinc carbonate. We tried several different temperatures and solutions but could not grow large crystals of zinc carbonate.

gypsum: Gypsum is relatively easy to dissolve in water, and precipitates as well formed monoclinic crystals. Larger crystals show growth striations and, if crystallization is rapid, show deformation features. Although both gypsum and kernite have distinctly different forms, they seem to precipitate in the same manner. It therefore might be intriguing to try solutions saturated in both to see what happens.

camphor and thymol: After crystallization, camphor has a quartz-like appearance. Crystals are subhedral, equigranular, and have low birefringence. Undulatory extinction is also apparent. The appearance is remarkably similar to a quartzite. In contrast, thymol produces feathery and radiating clusters of crystals with higher birefringence.

Conclusion

The experiments described above, and many other similar ones, provide a simple way for students to see crystallization in action. Many different compounds, forming many different kinds of crystals, can be studied. The equipment is easily obtained, the costs are low, and the experiments can be completed in short time.

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MINERAL SYNTHESIS AND X-RAY DIFFRACTION EXPERIMENTS

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GENERAL INSTRUCTIONS, COMMENTS AND NOTES

Purpose:

- give students a better understanding of how and why mineralogical reactions occur
- give students a practical introduction into the use of an X-ray diffractometer
- teach students to be creative, critical and analytical in the face of confusing or ambiguous data
- give students an understanding of, and appreciation for, the way scientists think and work

Philosophy:

These labs are based on experimentation, but if they are to be valuable learning experiences, instructors should avoid the “cook book” approach to science. We give students assignments/problems with only a minimum of instruction. The goals are clearly set out, but the means are not. Sometimes, experiments may not “succeed,” no matter what students do. In others, the results depend on the techniques used or on student ingenuity. Ambiguous results are common. It is tempting for instructors (especially graduate students teaching assistants) to try to put students on the “right path” by explaining too much. If you do that, it stifles student creativity and thinking and leads to student boredom. If you let them operate on their own, they will amaze you.

Although we may give individual students individual assignments, we encourage them to work in groups--one way to do this is to have half their grade come from their own work, and the other half from the group's work as a whole. We often have groups of 3-4 students, with each working on their own individual mineral. We group them by mineral chemistry.

Although students are sometimes confused or uncertain, after completing the mineral experiments, most of our students give “a big thumbs-up.” Some really excel at this sort of exercise. Sometimes the best students are ones who only receive mediocre scores on traditional labs or exams. At the other extreme, we have found that a few students cannot handle the uncertainty involved in true experimentation. No matter how we explain and encourage, they are frustrated at not knowing how to do things, and at not getting what they think is the “right” answer. They seem unwilling to make, or incapable of making, meaningful interpretations. Most of the frustration seems to stem from lack of confidence.

Specific Projects:

We have had our students try to synthesize many different minerals in many different chemical systems. It really makes no difference which minerals students try to make, because it does not matter if their experiments succeed. In fact, the students often gain more from these exercises if they have to explain why things apparently “failed.” But, if you want experiments that give the expected results, have them try making spinel minerals (spinel, galaxite, etc.)--just about any spinel mineral will yield good results. (You can incorporate Fe as Fe_2O_3 --it will partially reduce to produce some spinels.) Pyroxene, olivines and calcium silicates (wollastonite, larnite, etc.) usually work out, but do not react as completely as oxides. They can also synthesize aluminosilicates and related minerals such as anorthite, grossular or andradite at one atmosphere,

but recycling is normally required to get large amounts of reaction. If you want to confuse/challenge students, have them try to make something that melts at relatively low temperatures--incongruent melting is the best if maximum confusion is what you are after. To avoid melting and some other problems, we recommend avoiding minerals containing K_2O or Na_2O .

As a variation on these labs, we have had students react two or three minerals to make another, or decompose a mineral and analyze the products. For example, they can react calcite with quartz to get a $CaSiO_3$ polymorph, or periclase with gibbsite to produce spinel. And, tremolite decomposes nicely to diopside+enstatite+quartz. In summary: try anything you feel like, just to see if it will work. Once you instill the right attitude in the students, all experiments become successful.

Library and Computer Resources:

Synthesis experiments have been done before, and if students poke around in a library they will find appropriate papers. Curiously, few students even think about going to the library. When they ask if it is OK, we encourage them to use library resources--some do, most do not.

Many good X-ray diffraction data bases and search programs are available. We find it better to have students use hard copies of X-ray reference files--even if that means that they are not doing "complete" searches. We use search manuals sometimes. Other times we print out 30-50 patterns and make copies available in the laboratory.

Some recommended chemicals to use as starting materials (reagent grade):

$CaCO_3$	Zn-acetate
MgO	Al-hydroxide
Fe_2O_3	MnO_2
TiO_2	silicic acid

Equipment Needed:

mortars/pestles	1000° oven
many small vials	ceramic crucibles
airplane glue	spatulas, scoops
balance scale (± 0.01 grams)	long handled crucible tongs
weighing paper	heat resistant glove
pelletizer	X-ray diffractometer
Teflon spray to lubricate pelletizer	

Handouts:

Attached to this write-up are lab handouts we used in 1997. Many variations are possible, and we make changes every year. In 1997, the students did their experiments over a six week period; they were doing other things in mineralogy lab at the same time.

Week #1: We instruct students about the need to write everything down in a lab book. This need cannot be overemphasized--students generally do not record things well enough so that they can go back later and figure out what they have done. We tell them to take care--especially with weighing--but inevitably they make mistakes. It is up to each instructor whether to point out the mistakes or let them go on and figure things out later.

We tell the students that, at high temperatures, compounds release H_2O and CO_2 and that simple reagents become oxides. We give them ceramic crucibles which they load with various pure reagents, weigh, and fire over night. After cooling, they reweigh the reagents and calculate the percent weight loss that each experienced. They compare results with theoretical ones based on chemical formulas. (These calculations are not trivial. Students may require a good deal of help and explanation. One problem is that the compositions of reagents such as Al-hydroxide and silicic acid usually do not correspond to those in books--as the students will find out! In addition, metal oxides such as MnO_2 may or may not be completely oxidized. And, calcium oxide picks up water from the atmosphere very quickly--actually gaining weight while it sits on a scale.) After everyone in the lab agrees on the "correct" weight loss percentages, students calculate the amounts of reagents they need to mix to synthesize their mineral. In the process they learn about converting moles to grams, etc.

Week #2: Students make their reagent mixes and collect X-ray patterns. They also X-ray each reagent individually, and the reagents that they fired at 1000°C the previous week. By comparing patterns, they can decide which peaks in their reagent "mix" pattern correspond to which reagents. Although not in the lab write-up this year, we also usually give them unlabeled X-ray patterns of natural samples of calcite, lime, periclase, gibbsite or diaspore, any Mn-oxide, and quartz to try to match with the patterns they collect. We ask them why the X-ray patterns for the reagents and the natural materials of similar composition do not match exactly. As reference materials, we give them copies of data from the JCPDS or another X-ray diffraction data base. Some results will be ambiguous. Students may need some guidance. They may need to be told how well peaks should match, how much attention to pay to peak intensities, and other practical things. But, as much as possible, they should be left alone to figure out what they think the best criteria are to establish a good match.

Week #3: Students grind their reagent mixes, make a pellet, and then put the pellet in a high-T oven. We use acetone to wet the powders, so the grinding is done under a hood or near an open window. They must be encouraged to grind for a long time (30 minutes is not unreasonable). Fine grinding is a key to good reaction! (The grinding process will result in big messes, and lots of spilling. That is one reason students started with a gram of material.) We make pellets by binding the powders (with airplane glue) in a homemade pelletizer made of tool steel. We have to go to the machine shop once a semester to get our pelletizer turned on a lathe because tool steel is easily galled. Although in a real research lab, researchers make pellets at high pressures, for student exercises high pressures should be avoided because of possible danger, and because the students will destroy cheap homemade pelletizers.

Students weigh empty crucibles, place their pellets inside, and then weigh the loaded crucibles. They place the crucibles into a cool oven which slowly heats to 800°C . Some samples partially crepitate on heating, which causes no problems. After cooking, students remove samples from the oven, reweigh them, and grind a small amount for X-ray diffraction. It is likely that students will get their samples mixed with someone else's!

Week #4: After students remove their pellets from the oven, they collect an X-ray pattern and identify the phases present. The amount of reaction depends on the compound they were trying to make and may not be great. They should compare their scan with the ones they collected for the dehydrated and decarbonated reagents--some peaks will likely match.

Week #5: Students now regrind their material, make new pellets, reweigh them, and recook them at 1000°C. For best results, they should repeat this process several times, but time may be a factor. In 1997 we did no repeats. Fine grinding is extremely important and often determines success or failure. After each cooking, a small amount of sample is reserved for X-ray diffraction. For some attempted syntheses, students obtain nearly complete reaction after one 1000 °C cycle. But for many compounds, recycling or higher temperatures are needed to get good reaction.

Normally we do not heat our ovens above 1000°C for several reasons. Hotter temperatures pose serious safety risks (but even 1000°C can give a bad burn if students do not take care); 1000°C ovens are not prohibitively expensive and are indestructible if treated reasonably; and most compounds do not melt at 1000°C. As a final “bonus” we sometimes have students submit their samples for cooking in a higher temperature oven (1300 or 1400 °C). This leads to much better reaction, and sometimes to melting (students never seem to think about melting as a possibility and are often confused when they get back a glass) with, perhaps, destruction of a ceramic crucible (which fortunately is not expensive).

Week #6: As a final report, we have each student group prepare an 8-10 page paper. Usually they include an additional 8-10 pages of X-ray diagrams. We ask them to analyze the diffraction patterns one-by-one, starting with the original mix and ending with the last attempted synthesis. We do not want students to get bogged down writing a “book,” but we want them to be able to summarize cogently what they have done and what happened. Students should, of course, be analyzing the results of their experiments at every step of the process. But, they will not without MUCH prodding. X-ray patterns should be collected and peaks identified after each cooking, because students should not go on if things are hopelessly confused or mixed up. Sometimes students may wish to start over. But, starting over is pointless if they are going to follow the same procedure, unless they made some fundamental error (e.g., weighing). They must, therefore, be encouraged to analyze their results and to figure out why they got what they did. Some experiments will not yield successful syntheses--they must understand that and explain why.

MINERAL SYNTHESIS PROJECT

Step 1: Formulas and Reagents

What are we doing for this lab?

For this lab you should do the following:

1. Start a lab notebook where you write down everything you do. Never throw anything away. Keep all notes and scribbles. Note any strange things that happen. Write it all down! When you do calculations or weigh things, have someone else check what you do and initial your notebook. This may sound hokey, but it pays off when things get confusing later on. I can't emphasize this enough. If you make errors or fail to write things down at the beginning, everything you do later will be worthless. Check and double check! I could tell you some embarrassing (but true) stories about times I didn't...don't write your own stories.
2. For each of the reagents you need to make your mineral, figure out how much oxide is in the reagent (see method below).
3. For your mineral, calculate how much of each reagent you need to mix to make a 1 gm equivalent mixture (see method below).

The easiest way (plan A) to make "synthetic minerals" might be to mix up pure elements, cook them together, and voila ==> a mineral. Unfortunately there are a zillion problems with this approach. The first one is that some elements are unstable or unavailable in their pure states. And, some of them are available but cost too much. So we consider plan B.

Plan B is to synthesize mineral from oxides. For example, hedenbergite has the formula $\text{CaFeSi}_2\text{O}_6$. We can write the following formula:



So, we could mix up 1 part CaO, 1 part FeO and one part SiO_2 (molar parts, not weight parts) and react them to get hedenbergite. But, guess what? CaO and FeO aren't available or stable.

So, we go to plan C. Your mission (plan C) is to synthesize your mineral from reagents available in the mineralogy lab. You will mix the appropriate amounts of TiO_2 , MnO_2 , CaCO_3 , Fe_2O_3 , $\text{Al}(\text{OH})_3$, MgO, silicic acid, and Zn acetate. Then you will pelletize your mix and fire it at high temperature. Today we will get you started on your mission, but it won't be completed for a while.

This is your project, but you have a partner and the final grade depends on both of your performances. Work with your lab partner, and consult with others in the lab as you go along. Maybe they have figured out some things you don't know. One important thing, however, is to remain skeptical. Don't believe anything anyone tells you unless you are convinced yourself. Figure things out for yourself because experimentation is not always like cook book chemistry labs. Things that are true for one student may not be true for others doing different experiments.

On the next page is a table with your starting ingredients listed. Note on reagents: they are never what they say they are. Unless you buy the most expensive reagents and store them in the best way, they will contain impurities. Absorbed water from the atmosphere is especially significant for some of them.

Table 1. Elements, oxides, and reagents in the Mineralogy Lab

element	oxide	reagent
Ti	TiO ₂	TiO ₂
Mn	MnO ₂	MnO ₂
Ca	CaO	CaCO ₃
Fe	Fe ₂ O ₃ (or FeO)	Fe ₂ O ₃
Al	Al ₂ O ₃	Al(OH) ₃
Mg	MgO	MgO
Si	SiO ₂	silicic acid
Zn	ZnO	Zn acetate

Calculations

First, you need to figure out what to mix up. The way to think about this is first to consider your mineral as made of oxide components. One mole of hedenbergite, our example, contains one mole of CaO, one mole of FeO, and two moles of SiO₂. We need to convert the molar values to weight percents. I have done this in the table below. The results (right hand column) are that a 1 gm mix of hedenbergite composition contains 0.22604 gm of CaO, 0.28959 gm of FeO, and 0.48436 gm of SiO₂. Now we just have to figure out how much CaO, FeO and SiO₂ are in the reagents we have available, and we can figure out how much reagent to use.

oxide	A= # moles oxide	B=formula weight of pure oxide (g/mole)	C=mass of oxide in our mix (AxB) (g)	X=weight % of oxide in our mix	W=weight of oxide in 1 gm of mix
CaO	1	56.08	c ₁ =56.080	X ₁ =c ₁ /Σc=22.604	W ₁ =0.22604 g
FeO	1	71.847	c ₂ =71.847	X ₂ =c ₂ /Σc=28.959	W ₂ =0.28959 g
SiO ₂	2	60.084	c ₃ =120.168	X ₃ =c ₃ /Σc= 48.436	W ₃ =0.48436 g
TOTAL			Σc=248.095	ΣX=99.999	ΣW=0.99999 g

Procedure for determining the oxide content of reagents

Warning: A 1000° oven is very hot! You can get burned easily. Use the long handled tongs and try to hide off to the side of the door. Wear the fire proof glove or you are a (burned) idiot. If you are intimidated, let the TA's do the hot work. That's why they make the big bucks.

Another Warning: Be sure to figure out (with a scratch or something) a way to identify your crucible. They all look the same after they come out of the oven.

Write all weights down in your lab notebook. Don't make mistakes! Carefully weigh an empty clean crucible. Add about 0.5 grams of reagent and weigh again. Calculate the weight of the sample in the crucible. Place crucible in oven for several hours or more. Remove and weigh as soon as it has cooled enough to handle and not hurt the scale. Now calculate the weight of the sample after firing (subtract the weight of the empty crucible). Assume that all the reagent has

reacted to the oxide (listed in Table 1). You can now figure out how much oxide is in the reagent:

$$\text{oxide \% in reagent} = 100 \times (\text{final weight of sample}) / (\text{starting weight of sample})$$

Iron poses a special problem. If we want reduced iron oxide (FeO) in our mix (as we do for hedenbergite), we need to make a correction if we start with oxidized iron oxide (Fe₂O₃). When we fire any iron oxide in air we get Fe₂O₃ (=FeO_{1.5}). The extra oxygen will (we hope) go away when we make our mineral. So, we need to put extra Fe₂O₃ in our mix to get the correct amount of FeO. The difference in the atomic weight of FeO_{1.5} and FeO is 11.13%. Hence, if we want FeO at the end, we need to add 11.13% extra Fe₂O₃. *Note: if we wanted Fe₂O₃ in our final product we would not add an extra 11.13%.* Its possible that the Fe₂O₃ will gain weight when fired. This could occur if some of the Fe is reduced. No problem. Do the calculation the same way.

For the sake of this example, we will assume that silicic acid contains 90.51wt% SiO₂, CaCO₃ contains 56.18 wt% CaO, and the Fe₂O₃ really contains 96.67 wt% Fe₂O₃. (These are typical values.) So, we calculate the amount of reagents in a 1 gm "hedenbergite" mixture:

oxide	grams of oxide needed = A	% of oxide in reagent/100 = B	Fe correction = C	total amount of reagent needed = A x C / B
CaO	W ₁ =0.22604 g	0.5618		0.40234 g
FeO	W ₂ =0.28959 g	0.9667	1.1113	0.33290 g
SiO ₂	W ₃ =0.48436 g	0.9051		0.53514 g
TOTAL	ΣW=0.99999 g			1.27038 g

So, our mix will weigh 1.27038 gm total. After firing we should have 1.00000 gm of product. But, since there is always some loss, we probably won't. But it should be close.

Step 2: Mixing Reagents and X-ray Analysis

What are we doing for this lab?

For this lab you should do the following:

1. Continue to write everything in your lab notebook.
2. Recheck your calculations and then mix up the appropriate reagents needed to make your mineral.
3. X-ray (and interpret the X-ray results):
 - a. reagents right out of the bottle
 - b. the dehydrated/decarbonated reagents (from last week)
 - c. your reagent mix prior to putting in the oven

Mixing Reagents

Once you have determined the amounts of reagents needed to make your mineral, it is time to mix them up. So here is the process I recommend. Determine how much of each reagent you need to make 1 gram of your mineral (you were supposed to do this last week, but you may want to redo it).

1. Zero the scale (no tare). Then weigh a piece of weighing paper without anything on it.

2. For each reagent: Put a different piece of weighing paper on the scale and tare to zero. Carefully weigh out the appropriate amount of reagent. Then carefully dump it onto the weighing paper you weighed in step 1. Do not spill. Don't make dust that blows away. Slowly, carefully, completely. **Do not put anything back into a reagent bottle--EVER!** Use small spatulas and go slowly.
3. When you get done weighing each reagent and combining them on one piece of weighing paper: zero the scale (no tare), weigh the loaded weighing paper, subtract the empty weight determined in step 1, and you will have the total weight of reagents in your mix. Check this total against your theoretical total. It should be close. If not, figure out why or do it all over again.

All weights, whether right or wrong, and all steps should be written down in your lab book! Have someone else check your weights at every step of the way!

Grinding that Mix

Now take your mix and put it into a mortar. Wet it with lots of acetone--so it is really swimming, not just damp--and grind for at least 10 minutes. 30 minutes is better. Make sure lab windows are open. Work under the hood with the fan on whenever you can. Add acetone as needed during the grinding process. Be careful when you first add acetone or you will "blow away" some of your mix and mess up the composition.

A description of what you mixed up and how you ground it should go in your lab notebook.

X-raying

The TA's will instruct you on the use of the X-ray machine. Please do it their way and don't break the machine or X-ray yourself. You should X-ray each of the reagents you are using (take sample right out of the bottle), the dehydrated reagents that you made last week, and your mix.

A description of how you prepare the samples and how you X-ray them should go in your lab notebook.

Analyze the Results

For the reagents: compare your X-ray results with reference data and scans provided by the TA's. For the dehydrated reagents: compare your results with reference data and scans provided by the TA's.

For your mix: Compare your scan with the scans for each individual reagent. Use colored pencils and color the various peaks that belong to each reagent.

Copies of your X-ray charts and data, and your interpretation go in your lab notebook.

Step 3: Pelletize and Start Cooking; Analyze X-ray Patterns of Initial Mixes

What are we doing for this lab?

For this lab you should do the following:

1. Continue to write everything in your lab notebook.
2. Grind your mix of reagents VERY well and then bind to make a pellet. Put the pellet in the 800°C oven and leave it there for a week.

Making Pellets

Once you have mixed the appropriate reagents, and ground the mix VERY well, it is time to make a pellet. To do this, put your powders in a mortar, add enough acetone to make it very wet, and then add a drop of glue. Mix well. Let it dry until just a bit moist. Put it in the pellet die and squeeze it between the two pistons. The TA's will show you how. Take care, the pellet die can be destroyed if you get the pistons in wrong or are sloppy about how you apply pressure. Depending on how moist your sample was, pressing of the powder should be real quick. Remove (or push out) one of the pistons. Then use the pushing tools (bolts) to push out the other piston and the pellet.

Cooking the Pellet

Place the pellet in a clean ceramic crucible and put it into the 800°C oven for a week. (Or get someone else to put it in there for you.)

A description of how you mixed and pelletized your sample and when and how you put it in the oven should go in your lab notebook.

Step 4: X-ray Products of 800° Oven

What are we doing for this lab?

For this lab you should do the following:

1. Continue to write everything in your lab notebook.
2. X-ray the products out of the 800° oven
3. Analyze X-ray pattern

Now is the time to start taking real care -- try not to lose any more of your sample or you will be in trouble later on!

Catch Up!

This week there is not a lot to do, so you can catch up if you are behind.

X-ray Product

Remove your pellet from the oven. Take your pellet and crush it. Probably you can do this in a mortar but maybe you will have to use a steel piston/cylinder. Grind your sample extremely well. Put a small amount on a glass slide for X-ray. Save the rest so you can make a new pellet later on.

X-ray your sample. Analyze the peaks. Compare the starting X-ray diffractions charts (for your mix and for the reagents separately) with your 800° chart. Also, be sure to compare the charts of the dehydrated/decarbonated reagents with your 800° chart. You should be able to match just about all peaks. If the reagents reacted to produce new phases, you may have to look up some peaks in the Search Manuals. The TA's will show you how. Of course, the goal was to synthesize your mineral--so be sure to check reference data for your mineral and compare to your experimental products. Good Luck! This can be confusing. Be patient and persistent and you will become enlightened.

Make sure copies of all diffractograms are in your notebook. And, also the details of your analysis of the pattern.

Step 5: Put Your Mineral in the 1000° Oven

What are we doing for this lab?

For this lab you should do the following:

1. Continue to write everything in your lab notebook.
2. Grind (very well) and repelletize your sample; put it in the 1000° oven

Hey-- It is even more important now to take real care -- try not to lose any more of your sample or you will be in trouble!

Make Another Pellet and Cook It

OK, now you have cooked your reagents at 800°. You have also X-rayed the products. Now, we want to recycle your stuff in a 1000° oven. So, take your products and crush them in a mortar. Take care not to lose any material. Grind extremely well and make a new pellet. Put it into the oven and relax.

Just as a reminder, you should now have the following X-ray patterns:

- (a) individual reagents
- (b) individual reagents after firing at 800°
- (c) starting mix of reagents
- (d) mix of reagents after firing at 800°

So, you can compare (a) with (b) to see what happens when reagents are cooked--you should be able to figure out what they change into. You can compare (a) with (c) to identify the X-ray peaks in your starting mix pattern. You can compare (b) with (d) to identify the X-ray peaks in your reagents after the first firing, and to identify what phases are present. You can also check to see if the mineral you are trying to make did indeed form.

Now, after we regrind, repelletize, and refire at 1000°, we will analyze the pattern again to see what happened. If we still aren't getting what we want, we may take new pellets over to the EERC and have them cooked at 1200°.

Step 6: X-ray Products of 1000° Oven

What are we doing for this lab?

For this lab you should do the following:

1. Continue to write everything in your lab notebook.
2. X-ray the products out of the 1000° oven
3. Analyze X-ray pattern

X-ray Product

Remove your pellet from the oven. Take your pellet and crush it. Probably you can do this in a mortar but maybe you will have to use a steel piston/cylinder. Grind your sample extremely well. Put a small amount on a glass slide for X-ray. Save the rest so you can make a new pellet later on. X-ray your sample. Analyze the peaks as you did for the products of the 800° oven.

Make sure copies of all diffractograms are in your notebook. And, also the details of your analysis of the pattern.

Prepare a Final Report as Instructed by the TA's.

MAKING SOLID SOLUTIONS WITH ALKALI HALIDES (AND BREAKING THEM)

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INTRODUCTION

When two cations have the same charge and a similar radius, a mineral that contains one of the cations may contain the other as well, thus forming a *solid solution*. Common examples include Mg^{+2} and Fe^{+2} as in olivine, Na^{+1} and K^{+1} as in alkali feldspar, Al^{+3} and Fe^{+3} as in garnet. Some solid solutions are complete, so minerals may occur with the similar cations present in any proportion (e.g. olivine). In other cases, the solid solution is limited (e.g. alkali feldspar) so that some intermediate compositions cannot be formed, at least at low temperatures. Solid solutions are important because the physical properties and behavior of a mineral depend on its chemical composition.

In this exercise, the class will grow a variety of crystals of the same mineral, but with different chemical compositions. These crystals will be made from mixtures of halite (NaCl) and sylvite (KCl) that are melted and cooled. Because K^{+1} is significantly larger than Na^{+1} , the unit cell is larger in sylvite than in halite. Intermediate compositions have intermediate unit cell sizes. Thus, a measurement of the lattice spacing of the crystalline products of your experiments can be used to determine their chemical composition. The principle goal of these experiments is to demonstrate that solid solutions do occur and that their physical properties vary with their chemical composition. Additional goals include studying the effect of composition on melting, exploring the process of exsolution as a function of temperature, and seeing the effect of fluids and deformation on crystallization kinetics.

SAMPLE PREPARATION

- The class should work together in small groups to prepare a series of ten-gram mixtures of NaCl and KCl in simple molar proportions, say every 10 or 20 mole percent KCl depending on the number of groups. Ten grams is much more sample than you will need, but the reagents are inexpensive and weighing larger quantities will improve the accuracy of the resulting mixes (Why?). Because the gram formula weights of these compounds differ ($\text{NaCl} = 58.4428$ g/mole, $\text{KCl} = 74.555$ g/mole), some calculation is required to determine the appropriate mass proportions. Both NaCl and KCl are hygroscopic, so for the most accurate results you should use dry reagents that have been heated above 100°C and cooled in a dessicator.
- Be sure to record your calculations and reagent weights in your lab notebook.
- Mix the measured NaCl and KCl thoroughly.

PART I. MAKING SOLID SOLUTIONS BY CRYSTALLIZING FROM A MELT

Many minerals grow by crystallizing from a magma. The compositions of the minerals generally reflect the compositions of the melt from which they have grown. Granites are rich in potassium and the feldspar that grows from granitic liquids is orthoclase. Gabbros are rich in calcium and the feldspar that grows from gabbroic liquids is Ca-rich plagioclase. By cooling quickly from a NaCl-KCl melt, you should be able to grow alkali halide crystals that have the same composition as the melt.

- Place a modest amount (1-2 grams) of your mixture in an inexpensive porcelain crucible with a shiny glazed finish.
- Wearing heat-resistant gloves and using tongs, carefully place the crucible with your sample in a box oven set at 800°C. Although the melting temperature varies with composition, this temperature should be hot enough to melt any sample except pure NaCl, which melts at 801°C. (You can put a sample of pure NaCl in the oven if you want to check the temperature. If any melting occurs, the sample and oven have reached temperatures of 801°C or higher. In fact, melting points of pure substances like NaCl are so consistent that they are used to calibrate thermocouples and other high temperature thermometers.)
- When your sample has melted (5-10 minutes), carefully remove the crucible (it's now at 800°C!) from the oven with the tongs and gloves. Set the crucible on a heat-resistant surface and let it cool. Initially, the NaCl-KCl mixture should be molten. However, it will crystallize in a few seconds, cooling rapidly because the sample is small -- much more rapidly than most igneous rocks. Crystallization is very fast in this system and the crystals will have grown from the melt at high temperatures (probably above 600°C). The sample and crucible will contract upon cooling, making cracking sounds.
- Be sure to wear eye protection if you want to watch the crystals grow.
- After the crucible has cooled, the alkali halide crystals can be easily removed from the crucible with a spatula.

X-RAY DIFFRACTION

The easiest way to examine the crystals you have grown is with powder x-ray diffraction -- if you have an x-ray diffractometer. The ionic radius of potassium (0.138 nm) is considerably larger than the ionic radius of sodium (0.102 nm), if both are in six coordination with chlorine. Halite (NaCl) and sylvite (KCl) have the same crystal structure (they are isostructural) based on a cubic closest packing of large Cl⁻ anions (radius = 0.181 nm) with the smaller cations (Na⁺ or K⁺) filling all the six-coordinated (octahedral) sites. In sylvite the chlorine atoms are farther apart, to accommodate the larger K⁺ ions, than they are in halite with its smaller Na⁺ ions. Thus, the d-spacing of each lattice plane (hkl) in sylvite is larger than the d-spacing of the same plane (hkl) in halite. If a crystal has a composition intermediate between that of NaCl and KCl, the d-spacing for any plane (hkl) should be intermediate between that of the same plane (hkl) in halite and sylvite. If the solid solution is ideal, then there is no ΔV of mixing and a graph of the d-spacing vs. molar composition should be a straight line.

- The crystals you have grown are surprisingly unstable at room temperature. Therefore, crush the sample lightly in a mortar. **Grind as little as possible!**
- Because of the high symmetry of halite, very few planes (hkl) give strong diffraction peaks. To speed the analysis, scan a small range of diffraction angles (2θ) from 27° to 33°. This range of 2θ should include the (111) peak for your samples. Remembering Bragg's Law ($n\lambda = 2d \sin \theta$), which mineral, halite or sylvite, would you expect to have the larger 2θ value for each peak?
- A scan rate of 1° 2θ per minute is normally sufficient. Slower or faster scan rates may give you more or less accurate peak positions, respectively.

DATA ANALYSIS

- Also, measure the position of the (111) peak on diffraction patterns for halite and pure sylvite.
- Draw a graph with d-values on the y-axis and molar composition (from NaCl to KCl) on the x-axis.
- Plot $d_{(111)}$ for each sample at the appropriate composition on this graph.

- Connect the data points for pure halite and pure sylvite with a straight line. Do the data points for the other samples fall on the line? If not, are they distributed randomly about the line or do they fall systematically above or below the line? Do these data demonstrate that you have grown crystals of composition between NaCl and KCl?

PART II. OTHER EXPERIMENTS

Precipitation from an Aqueous Solution

- Both halite and sylvite are highly soluble in aqueous solutions. Dissolve 1-2 grams of your NaCl-KCl reagent mix in 10-20 cc of distilled water, stirring well.
- Evaporate the solution and collect powder x-ray diffraction data on the precipitate that remains.
- Explain your results.

Effects from Grinding

- Prepare a solid solution sample from an alkali halide melt as described in Part I and collect x-ray data after a light crushing.
- Grind the sample vigorously in a mortar and then collect x-ray data.
- Explain your result.

Effect of Water

- Prepare a solid solution sample from an alkali halide melt as described Part I and collect x-ray data after a light crushing.
- Grind the sample gently, but add a few drops of water to the mortar.
- Collect x-ray data and explain your result.

Melting Temperature

- Measure the melting temperature for a series of alkali halide crystals ranging in composition from pure NaCl to pure KCl.
- Graph the measured melting temperatures as a function of composition in the NaCl-KCl system.
- Your answer may differ if you start with a halite-sylvite mixture or with an alkali halide solid solution crystal prepared as in Part I. Why?

Breaking Solid Solutions

- Prepare a suite of solid solution samples from an alkali halide melt, as described Part I, and collect x-ray data after a light crushing.
- Anneal the samples in a 450°C oven (for 15 minutes?).
- Collect x-ray data on your sample and explain what you see.
- Repeat this experiment at other temperatures (350-500°C ?).
- Graph your data.
- Compare your results to the alkali feldspar phase diagram.

REFERENCES

- Barrett, W.T., and Wallace, W.E. (1954) Studies of NaCl-KCl solid solutions. I. Heats of formation, lattice spacings, densities, Schottky defects and mutual solubilities: *Journal of the American Chemical Society*, 76, 366-369.
- Levin, E.M., Robbins, C.R., and McMurdie, H.F. (1964) *Phase Diagrams for Ceramists: The American Ceramic Society, Columbus*, 601p.

NOTES TO THE INSTRUCTOR

These experiments are quite easy and satisfying to perform. The kinetics of crystallization, nucleation and growth, exsolution, and diffusion are quite rapid in the NaCl-KCl system, so quite a few experiments can be performed during one lab session. Because x-ray diffraction data is needed only for a 6° range in 2θ , characterization of the run products also can be completed quickly. The first part of the exercise as I have described it is very structured. Part II is less structured and more open-ended. Alternatively, you can design an exercise that gives the students less guidance and lets them discover for themselves the details of the NaCl-KCl phase diagram. However, because alkali halide crystals of intermediate composition are notoriously unstable at room temperature, I suggest that you at least warn students of this fact and give them guidance in preparing their samples for x-ray diffraction. When I first tried these experiments, I had some puzzling results due to grinding and also due to getting the sample damp while trying for a more rapid quench (hot ceramic crucibles crack if you set them in a pan of water!). Then I read that some of the chemists trying similar experiments (e.g. Barrett and Wallace, 1954) worked in a dry box to get consistent results! The following figures are the results of experiments with two different classes. The data are surprisingly good with minimal effort and care.

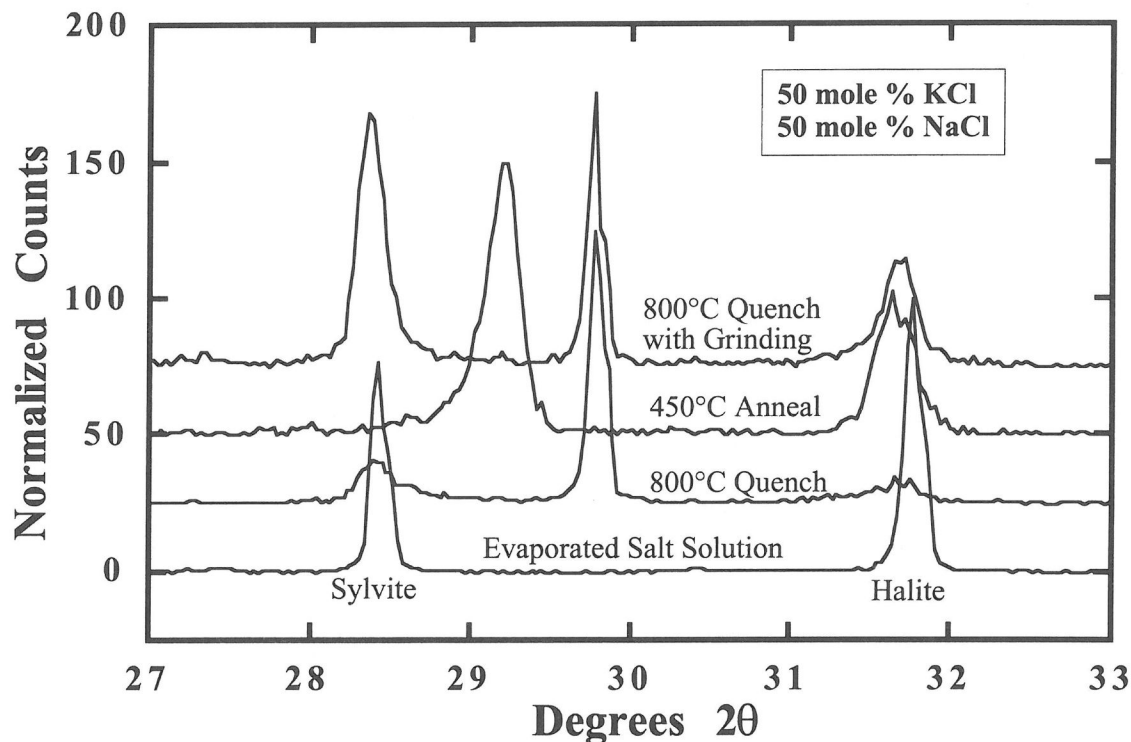


Figure 1. Class x-ray diffraction data for four experiments with a 50:50 KCl-NaCl mix. All peaks are for the (111) plane of sylvite, halite, or an alkali halide solid solution. The bottom line, which shows the location of the (111) peak for halite and sylvite, was obtained from a sample precipitated from an aqueous solution upon evaporation. The second line is for a nearly homogeneous solid solution sample quenched from an 800°C molten salt solution. The third line is for a sample that was first quenched from a melt and then held at 450°C for 24 hours. The two peaks show that both a potassium-rich and a sodium-rich alkali halide phase are present. The top line is for the quench sample of the second line that has been ground a short time in a mortar. Sylvite and halite peaks have appeared due to recrystallization during grinding.

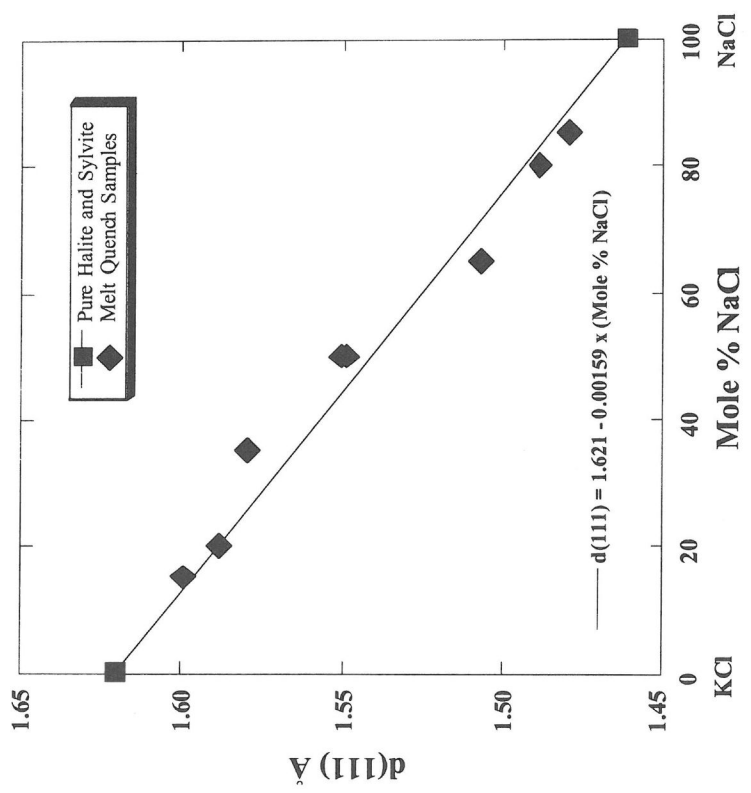


Figure 2. Class x-ray diffraction data for alkali halide solid solution samples quenched from alkali halide melts. The chemical composition of the melt mixture is given on the horizontal axis. The measured $d_{(111)}$ of the quenched products is given on the vertical axis. The line connects the observed $d_{(111)}$ values for sylvite and halite.

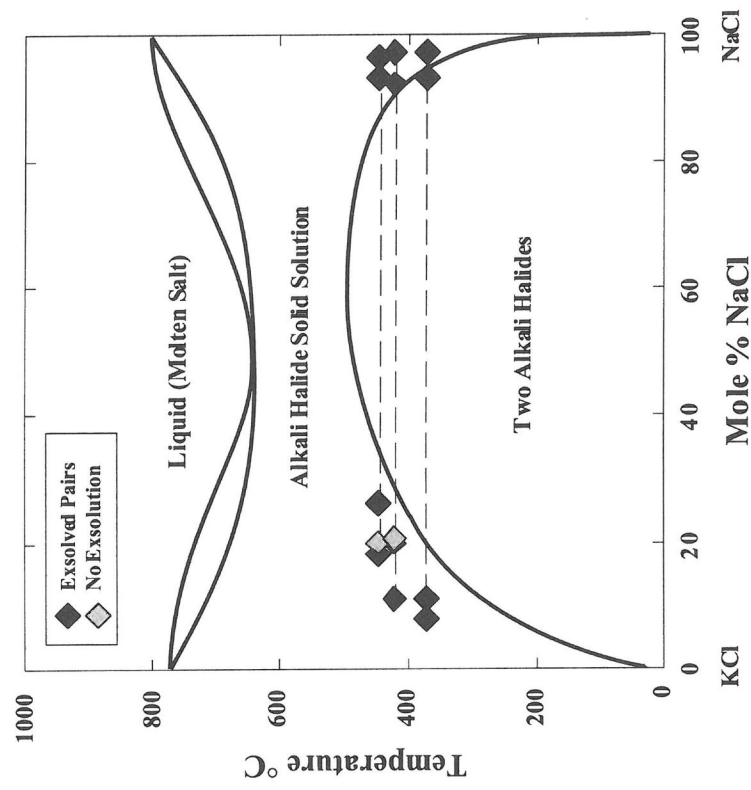


Figure 3. Class exsolution data for annealing of samples quenched from alkali halide melts. The dashed lines connects the observed alkali halide pairs. Two samples that did not exsolve are also shown. Compositions are based on measured $d_{(111)}$ values and the line in Figure 2. The solvus is from Barrett and Wallace (1954). The liquidus and solidus are schematic, but are based on the melting points of sylvite and halite and Figure 1258 in Levin et al. (1964).

PHASE FUN WITH FELDSPARS: SIMPLE EXPERIMENTS TO CHANGE CHEMICAL COMPOSITION, STATE OF ORDER, AND CRYSTAL SYSTEM

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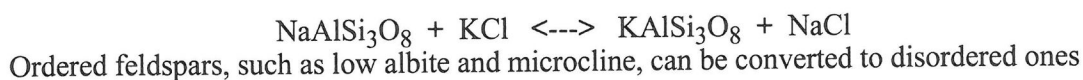
INTRODUCTION

Alkali feldspars form solid solution series ranging in chemical composition from KAlSi_3O_8 to $\text{NaAlSi}_3\text{O}_8$. In addition to K-Na chemical substitution, these minerals vary in the way aluminum (Al) and silicon (Si) ions are distributed among the symmetrically nonequivalent tetrahedral sites that make up their structures (Figs. 1 and 2). Two distinctly different kinds of distributions can be found. In low albite ($\text{NaAlSi}_3\text{O}_8$) and microcline (KAlSi_3O_8), both of which have triclinic symmetry, Al and Si are distributed among four symmetrically distinct tetrahedral sites (named T10, T1m, T20, and T2m), and most of the Al ions are concentrated in only one of these, Si filling the other three (a so-called "ordered" distribution). In analbite ($\text{NaAlSi}_3\text{O}_8$) and sanidine (KAlSi_3O_8), however, Al and Si are more-or-less randomly distributed ("disordered") between just two tetrahedral positions, T1 and T2 (the "0" and "m" positions having become symmetrically equivalent through mirror plane and rotational symmetry). Moreover, analbite and sanidine possess "topochemically monoclinic" Al-Si distributions, i.e., tetrahedral site occupancies consistent with monoclinic symmetry; this is not the case for low albite and microcline.

Despite the fact that analbite and sanidine have topochemically monoclinic Al-Si distributions, only the unit cell of sanidine has true monoclinic geometry at room temperature (although analbite can be converted to monoclinic geometry by heating to about 980°C). Relative to K-rich sandine, the smaller sodium ion in analbite causes a so-called displacive phase transformation that converts the structure to triclinic symmetry. Low albite and microcline, therefore, are triclinic for a different reason than analbite. The former minerals have Al-Si distributions that are inconsistent with monoclinic symmetry. The unit cell of analbite, on the other hand, is metrically triclinic due to Na.

In addition to the end members, some natural alkali feldspars have intermediate chemical compositions and Al-Si distributions. Virtually no naturally occurring "potassium feldspar" is devoid of sodium. And the potassic feldspar "orthoclase" has a monoclinic Al-Si distribution similar to that of sanidine, but with Al more abundant in the T1 site than in T2. For the purposes of this exercise, however, we shall focus only on the four end members: Low albite, microcline, analbite, and sanidine.

Sodium feldspars (low albite and analbite) can be converted to potassium feldspars (microcline and sanidine, respectively), or vica versa, through simple short-term "ion-exchange" experiments. This chemical conversion can be achieved easily by immersing feldspar grains in molten salts such as KCl, NaCl, KBr, or NaBr. In such experiments the feldspar grains exchange alkali ions with the molten salt according to reactions such as



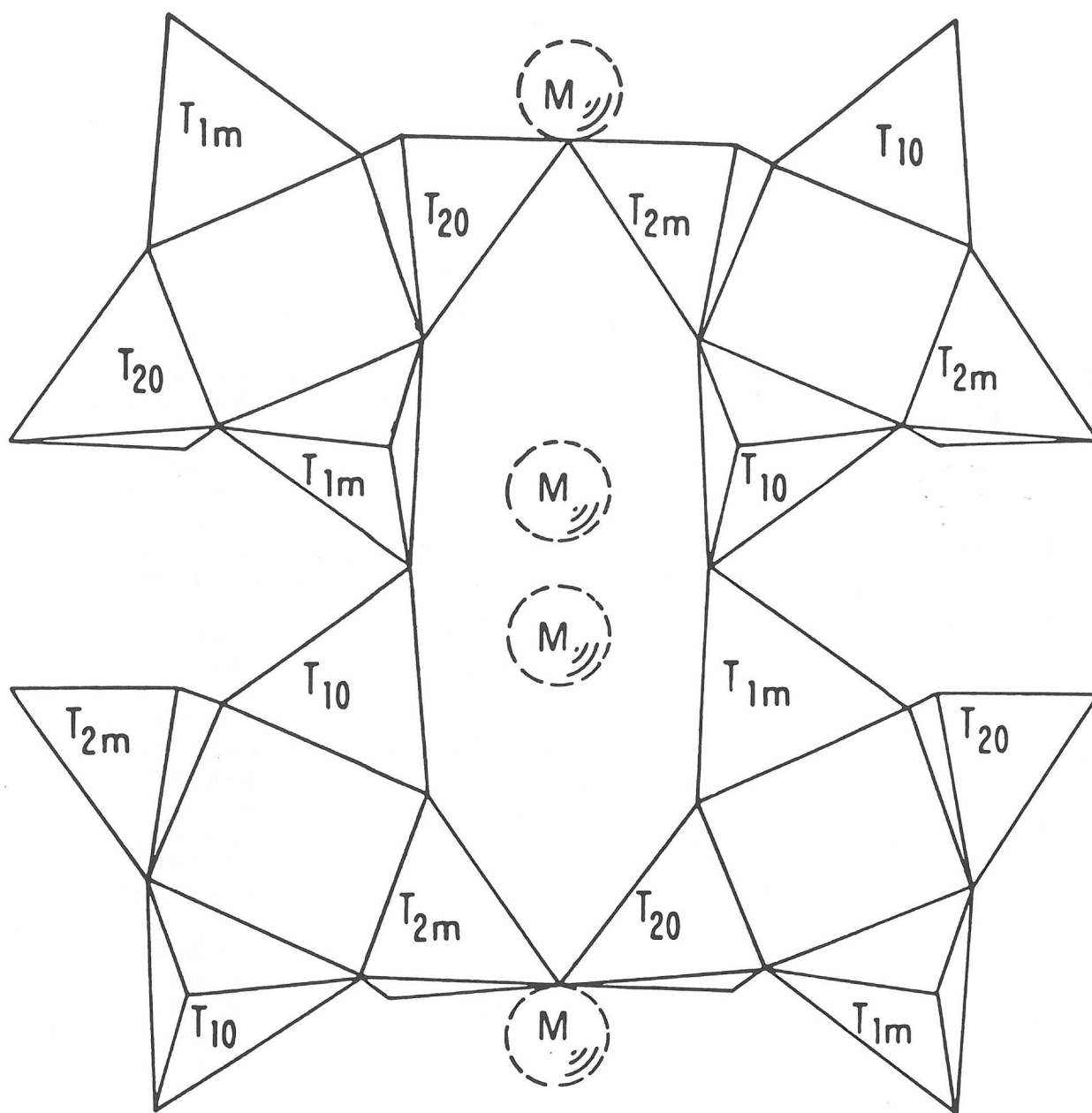


FIGURE 1. A portion of the triclinic alkali feldspar structure projected onto the $(\bar{2}01)$ crystallographic plane. Symmetrically distinct tetrahedra are indicated by T10, T1m, T20, and T2m labels. The positions of alkali ions are designated "M."

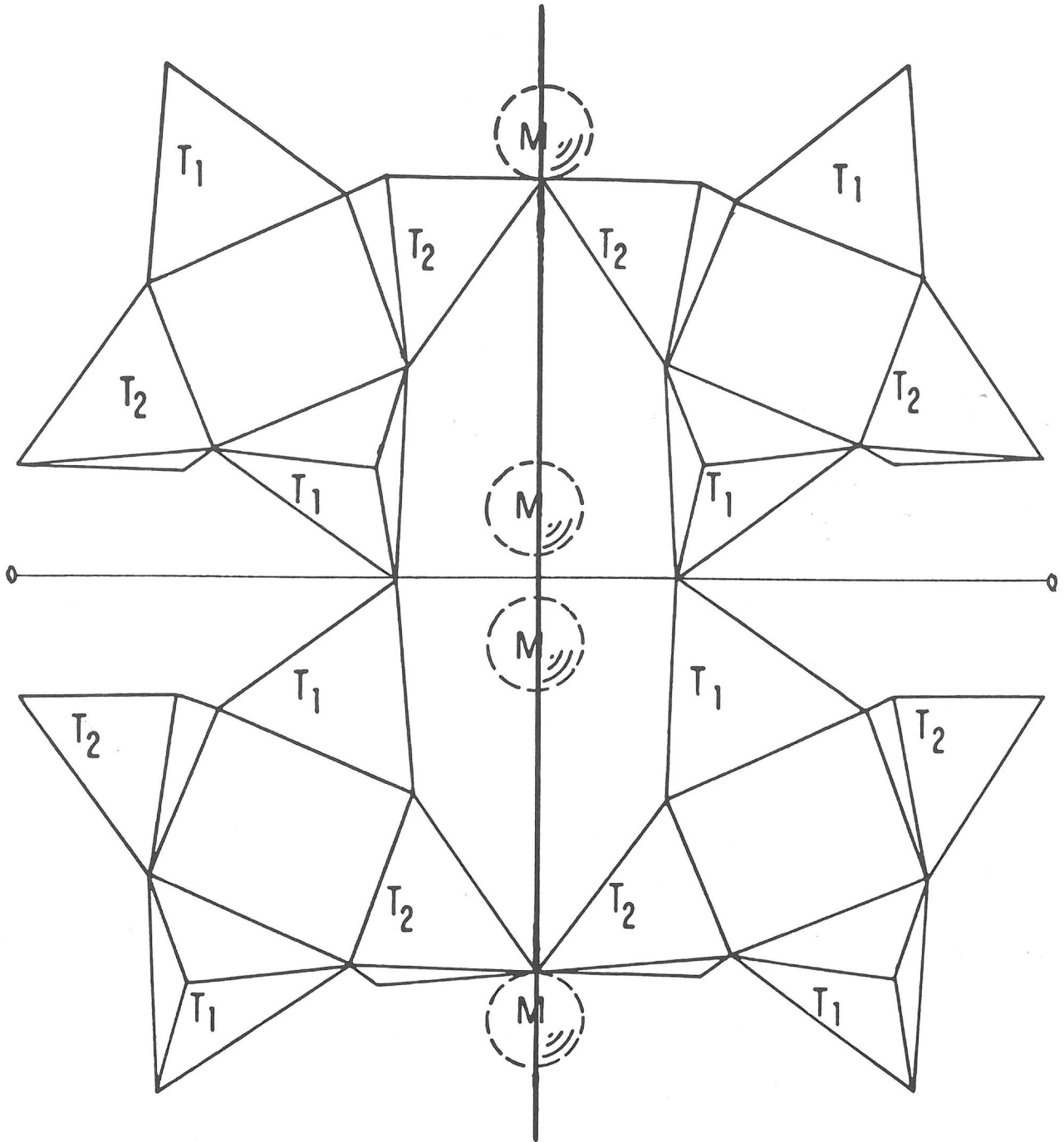


FIGURE 2. A portion of the monoclinic alkali feldspar structure projected onto the $(\bar{2}01)$ crystallographic plane. Symmetrically distinct tetrahedra are labeled T_1 and T_2 . Tetrahedra that had "O" and "m" designations as triclinic feldspars are symmetrically related in monoclinic feldspars by a mirror plane (heavy line) and a two-fold rotational axis (light line) perpendicular to the mirror plane. Thus, the number of distinct tetrahedral sites is reduced from four to two.

(analbite and sanidine, respectively) through long-term heating experiments that cause Al and Si to exchange places among the tetrahedra. Remember, even though analbite is metrically triclinic, its Al-Si distribution is disordered and consistent with monoclinic symmetry, so it can easily be transformed to true monoclinic geometry through potassium-exchange and conversion to sanidine. Relationships among the four end members are summarized as follows:

ORDERED ALKALI FELDSPARS
(TOPOCHEMICALLY AND METRICALLY TRICLINIC)

LOW ALBITE *****MICROCLINE	
(TRICLINIC)	(TRICLINIC)
*	*
*	*
*	*
*	*
SODIUM	* POTASSIUM
FELDSPARS	* FELDSPARS
*	*
*	*
*	*
*	*
*	*
ANALBITE *****SANIDINE	
(METRICALLY TRICLINIC)	(METRICALLY MONOCLINIC)

DISORDERED ALKALI FELDSPARS
(TOPOCHEMICALLY MONOCLINIC)

DATA COLLECTION

Each student should obtain an “unknown” feldspar end member from her/his instructor. Prepare the specimen for X-ray diffraction analysis, then collect X-ray data over a 2θ range from about 18° to 60° (if you are not using $\text{CuK}\alpha$ radiation, your instructor will adjust these values).

X-Ray Data Analysis: There are significant differences among the X-ray diffraction patterns of the four alkali feldspar end members. Data for these can be found in Borg and Smith (1969; note that these authors refer to analbite as “high albite”). To become familiar with the differences among the patterns, you might first compare end-member X-ray data for the low-angle 2θ region (18° to 35°). Figures 1 and 2 in Hovis (1989) also can be helpful.

Composition Determination: Alkali feldspar composition is expressed by N_{Or} , the mole fraction of K in the mineral (e.g., if $N_{\text{Or}} = 0.9$, the feldspar formula is $\text{K}_{0.9}\text{Na}_{0.1}\text{AlSi}_3\text{O}_8$). The (201) X-ray peak position varies nearly linearly with N_{Or} (Fig. 3) between 2θ values of about 21° for K-feldspars ($N_{\text{Or}}=1$) and 22° for Na-feldspars ($N_{\text{Or}}=0$). Find this peak and record its position.

- A. Use Figure 3 to graphically approximate the chemical composition of your specimen from the position of its (201) X-ray diffraction peak (or calculate composition from the equation given in the figure caption). Is your feldspar sodic or potassic?

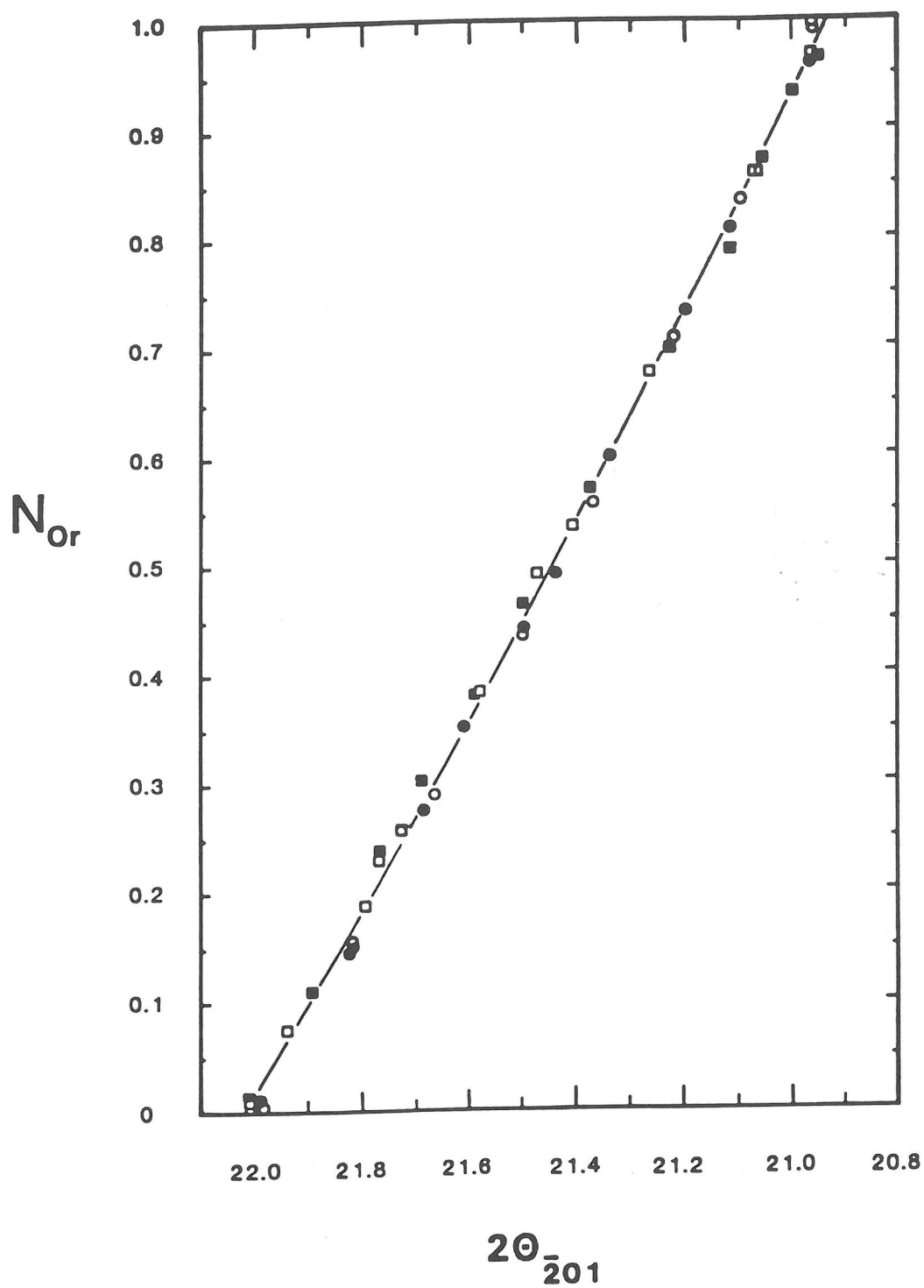


FIGURE 3. Plot of N_{Or} against 2Θ for the $(\bar{2}01)$ X-ray diffraction maximum ($\text{CuK}\alpha$ radiation; Hovis, 1989). Data points are for feldspars with a wide range of Al-Si distributions. Compositions may be determined either graphically or by using the equation for the curve above: $N_{Or} = 70.726 - 5.6200 (2\Theta) + 0.10936 (2\Theta)^2$.

State of Al-Si Order: You can obtain an estimate of the Al-Si distribution in your alkali feldspar by comparing your X-ray data to those for the pertinent end members. You know from Part A whether your feldspar is sodic or potassic. Now compare your X-ray pattern to those of the appropriate end members in Borg and Smith (1969), low albite and analbite if your specimen is sodic, or microcline and sanidine if your specimen is potassic.

B. Which of the end-member X-ray patterns comes closest to matching your data?

Another measure of Al-Si distribution is based on the difference in the positions (2θ 's) of the (131) and (1 $\bar{3}$ 1) X-ray peaks. Kroll and Ribbe (1983) have summarized $\Delta(2\theta)$ [(131) - (1 $\bar{3}$ 1)] values for the four alkali feldspar end members as follows: Low albite (+1.10°), analbite (+2.00°), microcline (-0.81°), sanidine (0.00°). [Sanidine is monoclinic, so its (131) and (1 $\bar{3}$ 1) peaks are equivalent.]

C. What is the difference in the 2θ positions of these peaks for your feldspar?

D. From this peak separation, and taking into account the chemical composition determined in Part A, what is the state of Al-Si order in your feldspar, "ordered" or "disordered?"

Experiments: Once you have obtained this baseline of information, try one or more of the experiments below and collect X-ray data from 18° to 60° on each product to see how the X-ray pattern has changed. After each experiment, determine the identity of the product by measuring the positions of the (201), (131) and (1 $\bar{3}$ 1) peaks. Also note whether there are other differences in the diffraction patterns that help in determining chemical composition and Al-Si distribution.

EXPERIMENTAL PROCEDURES

Low Albite ---> Microcline

1. Grind low albite into a powder (fine enough to pass through a 200-mesh sieve).
2. Place the powder in a crucible appropriate to the temperature of this experiment (Pt works well but others may work also) containing a large excess of KCl. (Use a molar ratio K:Na > 100:1. Three grams of chloride for every 0.1 gram of feldspar will accomplish this.)
3. Mix the feldspar powder with the KCl.
4. Place a lid on the crucible.
5. Place the crucible in a box oven and increase the temperature to 30° above the melting point of the KCl (776°C + 30°C = 806°C). [**Warning:** Do not use research-grade equipment for this, because to a small degree evaporating KCl will contaminate the oven.]
6. Leave the crucible in the oven for 24 hours.
7. Remove the crucible from the oven (either at high temperature or after it has cooled). Cool to room temperature.

8. Place the resulting feldspar and chloride in distilled or deionized water (if the outside of the crucible is clean, you can simply place the entire crucible in a beaker and fill it with water). After some chloride has dissolved, pour off the solution (be careful not to lose feldspar), and add more water. Several rinsings will be required to remove all chloride; if you do not succeed in doing so, you will get both feldspar and chloride peaks in the X-ray spectrum.
9. Discard the final solution and dry the feldspar.

Microcline ---> Low Albite

1. Use the same procedures as above, but with microcline as the starting material, NaCl (melting temperature of 801 °C) as the exchange medium, and an oven temperature of about 830°C.
2. One difference between this ion exchange and the one above is that conversion of low albite to microcline cracks the feldspar (from expansion), whereas this reaction will not. So in the first case, if you do not grind the feldspar fine enough, the ion exchange will likely go to completion anyway. But in the microcline ---> low albite conversion, a coarse initial sample probably will result in an inhomogeneous final product (K-rich grain cores).

Low Albite ---> Analbite

1. Anneal low albite powder or a crystal at 1050°C. Several days (five) is probably enough time for conversion to analbite, but two or three weeks will guarantee success.

Microcline ---> Sanidine

1. Use the same procedure as low albite ----> analbite. In this case, however, you really will need three weeks at 1050°C to guarantee success, since this transformation is more sluggish than for the sodic analogs.

Analbite ---> Sanidine and Sanidine ---> Analbite

1. Use the same procedures as for low albite ---> microcline and microcline ---> low albite, respectively.

“Around the World”

1. If you want to be bold, try making all four phases starting with a single mineral. First convert microcline to low albite, then disorder the low albite to form analbite, then potassium-exchange the analbite to make sanidine! Or use the reverse route: low albite ---> microcline ---> sanidine ---> analbite. [Note: You will not be able to complete the circuit to the ordered phase, since disordered feldspars cannot be made to “reorder” in reasonable periods of time under dry conditions.]

Intermediate Compositions

1. You also can make intermediate compositions between low albite and microcline or between analbite and sanidine. Combine powders of the end-member phases in the molar proportions desired to synthesize the composition you want. [To do this you will have to think about how weights of the samples are related to moles.]
2. Mix the powders well (doing it in a fluid such as acetone helps), then pack the dry powders tightly into a crucible. [It helps to make a pellet using a pelletizer or to tamp down the powders with a bent spatula to promote as much grain-to-grain contact as possible.]
3. Place the crucible in a box oven and increase the temperature to 930°C.
4. The feldspar grains will chemically homogenize after about five days. It will help if you remove the crucible from the oven every 24 to 48 hours and remix the sample. This will aid ion exchange of K and Na between grains.
5. Remove the crucible from the oven while at high temperature. [This will require a pair of long-handled temperature-resistant tongs.] Allow the crucible to cool on a well-insulated bench top. A homogeneous K-Na feldspar should result.
6. Since K-Na substitution causes all X-ray peaks to shift positions, it will be difficult to compare X-ray data for intermediate compositions to those of end-member feldspars. However, even for these feldspars chemical composition can easily be determined through use of the (201) peak/line (Fig. 3). Once composition has been established, data for additional peaks can be matched to those in Figures 1 and 2 of Hovis (1989).

FURTHER ANALYSIS OF STRUCTURAL STATE

For topochemically monoclinic feldspars a number of peak separations, some largely independent of composition [e.g., (204)-(060) and (060)-(113)], can be used to measure the degree of Al-Si order-disorder (see Figs. 3 through 6 of Hovis, 1989). Unit-cell dimensions also can be utilized to characterize composition and Al-Si distribution (see Hovis, this publication).

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NOTES TO THE INSTRUCTOR

For starting materials you can use natural low albite, microcline, or sanidine. If you want to use analbite, you will have to synthesize it using techniques described in the text. Sanidine also can be synthesized from either microcline or orthoclase through disordering experiments.

If your students are confused by the details of order-disorder relationships, do not be discouraged from running the lab; there are still lots of things you can do. It is enough for them to understand that there are differences among alkali feldspars in Al-Si distribution and that these are related primarily to temperature of equilibration.

There are a variety of ways that you can run this lab. For example, you could give different end members to different class members and have each identify the initial specimen. Then, you could assign each student (or group) an experiment, either ion exchange or disordering, and have them identify the final products. Note, however, that you will not be able to reorder disordered specimens.

Or you could give all class members the same initial mineral (preferably an ordered one), then have different students (groups) perform different experiments on it. Some students may want to do the whole "Around the World" tour.

Dexter Perkins has told me that he has students do time-based experiments to demonstrate kinetics. So one could run ion-exchange experiments for shorter periods of time (or with larger grain sizes) to demonstrate inhomogeneity of the final product (broad, or double, (201) peak). One could do the same thing with disordering experiments. Dexter also indicated that he has his students do comparative chloride melt experiments using CaCl_2 as an exchange medium, then asks them to figure out why virtually no ion exchange with the feldspar took place.

You also can try ion exchange in mixed salts [e.g., $(\text{K},\text{Na})\text{Cl}$], but you should be forewarned that the resulting feldspar will not have the same composition as the initial salt, even if you swamp the system with salt. The alkali feldspar - $(\text{K},\text{Na})\text{Cl}$ system forms a "reciprocal ternary," but the tie lines do not connect feldspar-salt pairs having the same K:Na ratio. A class project might be to figure out the configuration of the reciprocal ternary tie lines. A word of warning, though: the achievement of equilibrium in such experiments takes significantly longer than 24 hours. One thing you can try here also is to approach the equilibria from both directions (reversed equilibria) using sodic and potassic feldspars and various salt mixtures as starting materials in different experiments.

Along the same lines as above, you can try ion exchange experiments between feldspars and salt below the melting point of the salt. Yes, feldspars and salts do exchange ions under these conditions, providing the temperature is not too low. If you do this below the critical temperature of the feldspar solvus, you could wind up with two feldspars and salt as a final product!

Let your imagination run wild. There are lots of possibilities. Have phase fun with feldspars!

DETERMINATION OF CHEMICAL COMPOSITION, STATE OF ORDER, MOLAR VOLUME, AND DENSITY OF A MONOCLINIC ALKALI FELDSPAR USING X-RAY DIFFRACTION

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INTRODUCTION

Alkali feldspars (commonly referred to as “potassium feldspars”) are among the most abundant minerals in the Earth’s crust. As such, they have the potential to provide important information about the rocks in which they occur. Using X-ray data, it is possible to characterize both the chemical composition and state of order of an alkali feldspar, and in some instances to approximate the temperature at which the feldspar equilibrated. Molar volume and density, fundamental properties of any mineral, also can be determined.

Although many chemical substitutions occur in these minerals, the replacement of K by Na is the most common. Thus, as a first approximation, alkali feldspars can be thought of as solid solutions varying from potassium-rich to sodium-rich end members, that is, from KAlSi_3O_8 to $\text{NaAlSi}_3\text{O}_8$. Mineralogists characterize alkali feldspar composition by a parameter called N_{Or} , which is simply the “mole fraction” of potassium in the mineral. If $N_{\text{Or}} = 0.7$, for example, a formula of $\text{K}_{0.7}\text{Na}_{0.3}\text{AlSi}_3\text{O}_8$ is implied (note that Na and K always add to 1.0). Both the a unit-cell dimension and the (201) X-ray diffraction peak of an alkali feldspar are quite sensitive to K:Na ratio. In this exercise both will be used to estimate the composition of an alkali feldspar.

In addition to chemical composition, alkali feldspars are characterized by their state of “order” or “disorder.” Ordering phenomena can occur in any crystalline material in which two or more ions compete for symmetrically nonequivalent crystallographic sites. In monoclinic alkali feldspars it is aluminum (Al) and silicon (Si) ions that occupy both of the crystallographically distinct tetrahedral sites (named T1 and T2; see Fig. 2 of Hovis, this publication). Ordering relationships, however, are found in many other mineral series, including pyroxenes, amphiboles, and micas, and in sites other than tetrahedral ones. Because these relationships are temperature- and/or pressure-dependent, they can give important information about the conditions under which a mineral has equilibrated.

The state of order in monoclinic alkali feldspars is defined by the distribution of Al and Si between the two tetrahedral sites. To illustrate, let us suppose that there are a total of 2000 tetrahedra in a tiny feldspar crystal. Since there are equal numbers of T1 and T2 sites, 1000 of these would be T1 sites and 1000 would be T2 sites. Because of the 1:3 Al:Si ratio, 500 Al ions and 1500 Si ions would occupy these sites. The most “ordered” possible monoclinic feldspar crystal would have all 500 Al ions in one site (the T1). The 1500 Si ions would fill the remaining 500 T1 sites and all 1000 of the T2 sites. Thus, the fraction of Al ions in the T1 site (symbolized $N_{\text{Al(T1)}}$) of such a crystal would be 0.50 (500/1000), and the fraction of Al in T2 ($N_{\text{Al(T2)}}$) would be 0.00. On the other hand, a “perfectly disordered” crystal would have a “random” distribution of Al and Si between the two sites (that is, the same occupancy in both sites). In such a case, 250 Al

ions and 750 Si ions would fill each site. In this case, $N_{\text{Al(T1)}} = N_{\text{Al(T2)}} = 0.25$ (250/1000).

A convenient way to express the Al-Si distribution of an alkali feldspar is with a single parameter, Z , defined as twice the difference of the atom mole fractions of Al in the two tetrahedral sites (Thompson, 1969 and 1970):

$$Z = 2 [N_{\text{Al(T1)}} - N_{\text{Al(T2)}}] \quad \text{Eqn. (1)}$$

Substituting into this equation the above mole fractions of Al, we see that a perfectly ordered monoclinic feldspar would have a Z -value of 1.0 (2 times 0.50), whereas a perfectly disordered one would have a value of 0.0 (2 times zero). Although we can relate the Z -values of any natural sample to this range (samples with Z -values closer to 1.0 being more ordered, and those closer to 0.0 more disordered), bear in mind that naturally occurring alkali feldspars seem to possess Z -values in a range from about 0.8 to 0.2; even synthetically disordered ones have Z -values of only 0.07 or so (Hovis, 1986). We can use X-ray data to estimate the Z -value of any monoclinic alkali feldspar.

Just as Z can be calculated from site populations, site populations can be calculated from Z . Considering Eqn. (1) above, and the fact that $N_{\text{Al(T1)}} + N_{\text{Al(T2)}}$ must sum to 0.5 in the simple K-Na alkali feldspar system, one can use these two simultaneous equations to demonstrate that

$$N_{\text{Al(T1)}} = (1 + Z) / 4 \quad \text{Eqn. (2)}$$

$$N_{\text{Al(T2)}} = (1 - Z) / 4 \quad \text{Eqn. (3)}$$

So, just as site populations can be used to calculate Z , Z -values can be converted to the fractions of aluminum (and silicon) in each of the tetrahedral sites. Whether one chooses a Z -value or the individual site populations to express the state of order is arbitrary; the two are equivalent.

For alkali feldspars, the state of order is almost solely dependent on the temperature of equilibration, ordered samples having equilibrated at lower temperatures (e.g., hydrothermal veins) than disordered ones (e.g., volcanic phenocrysts). Because geologists are interested in the conditions to which a rock has been exposed, the temperature information that a feldspar-bearing rock might provide is potentially valuable. One must remember, however, that feldspars can re-equilibrate (become more ordered) as they cool; the environments most likely to have preserved temperature information are either those in which cooling occurred rapidly under relatively dry conditions, or ones in which temperatures never were very high.

DATA COLLECTION

Each student should obtain a monoclinic alkali feldspar from the instructor and prepare the sample for X-ray analysis. If students have been instructed on the use of an "internal standard" (silicon makes a good one), include it in the sample, otherwise ignore the internal standard. If you do not use an internal standard, however, your X-ray system must be relatively well aligned, because errors in 2θ will produce errors in both peak positions and unit-cell dimensions.

1. If using $\text{CuK}\alpha$ radiation, collect X-ray data from 18° to 60° 2θ . If using another type of radiation, adjust these values appropriately. If using a diffractometer, a scan rate of $1^\circ/\text{min}$ produces better data, but rates up to $5^\circ/\text{min}$ may be employed.

2. Measure and record the positions and intensities of as many peaks/lines as possible. If an internal standard was mixed with the sample, correct all peak positions using data from the standard.
3. Identify the Miller Indices of each peak/line. The data in Borg and Smith (1969) for adularia, orthoclase, and sanidine will be helpful. If you cannot determine which of the latter data sets is most closely comparable to yours, index peaks using the data for orthoclase. Peaks also can be indexed using information in the JCPDS data base.
4. Using a lattice constant refinement program such as LCLSQ (Burnham, 1962), or the "electronic spreadsheet" of Novak and Colville (1989) or software included with an automated X-ray system, compute the unit-cell dimensions of your sample. In making this calculation, you should ignore "overlapping" peaks/lines (i.e., those for which there is more than one set of Miller Indices) should be ignored. Remember to refine the unit-cell dimensions in the monoclinic crystal system.
5. Record the position of the ($\bar{2}01$) peak, found in the general vicinity of $21^\circ 2\theta$ for $\text{CuK}\alpha$ radiation.

PART I: COMPOSITION DETERMINATION

Remember that the principal chemical substitution in alkali feldspars is $\text{K} = \text{Na}$. As larger potassium ions replace smaller sodium ions, the interplanar spacings (d_{hkl}) generally increase, and as a result all three of the unit-cell axes (a , b , c) expand. Of these a is the most sensitive to composition (Fig. 1). Furthermore, as any one interplanar spacing increases, the corresponding 2θ decreases (a function of the Bragg equation). As an individual peak/line, the ($\bar{2}01$) is especially sensitive to $\text{K} = \text{Na}$ substitution, changing from about $22^\circ 2\theta$ for pure-Na feldspar to 21° for pure-K feldspar ($\text{CuK}\alpha$ radiation; see Fig. 3 of Hovis, this publication).

- A. Use the ($\bar{2}01$) peak of your feldspar and the equation below (Hovis, 1989) to compute N_{Or} . (Values of 2θ should be for $\text{CuK}\alpha$ radiation.)

$$N_{\text{Or}} = 70.726 - 5.6200 (2\theta) + 0.10936 (2\theta)^2 \quad \text{Eqn. (4)}$$

- B. Substitute the a unit-cell dimension of your feldspar into the equation below (Hovis, 1986) as a second method of computing N_{Or} ; this should produce a value similar to that in Part A.

$$N_{\text{Or}} = -366.3261 + 129.2335 a - 15.42053 a^2 + 0.6232109 a^3 \quad \text{Eqn. (5)}$$

- C. The two methods will not compare perfectly, but they should be close. How well do the two N_{Or} values agree?
- D. If they do not agree well, what might be the reason(s)?

PART II: DETERMINATION OF STATE OF ORDER

Just as with composition, peak positions and unit-cell dimensions are affected by the interchange of Al and Si ions between T1 and T2 tetrahedral sites. At any one composition, disorder causes the c dimension to shorten and the b dimension to lengthen. A plot of c against b

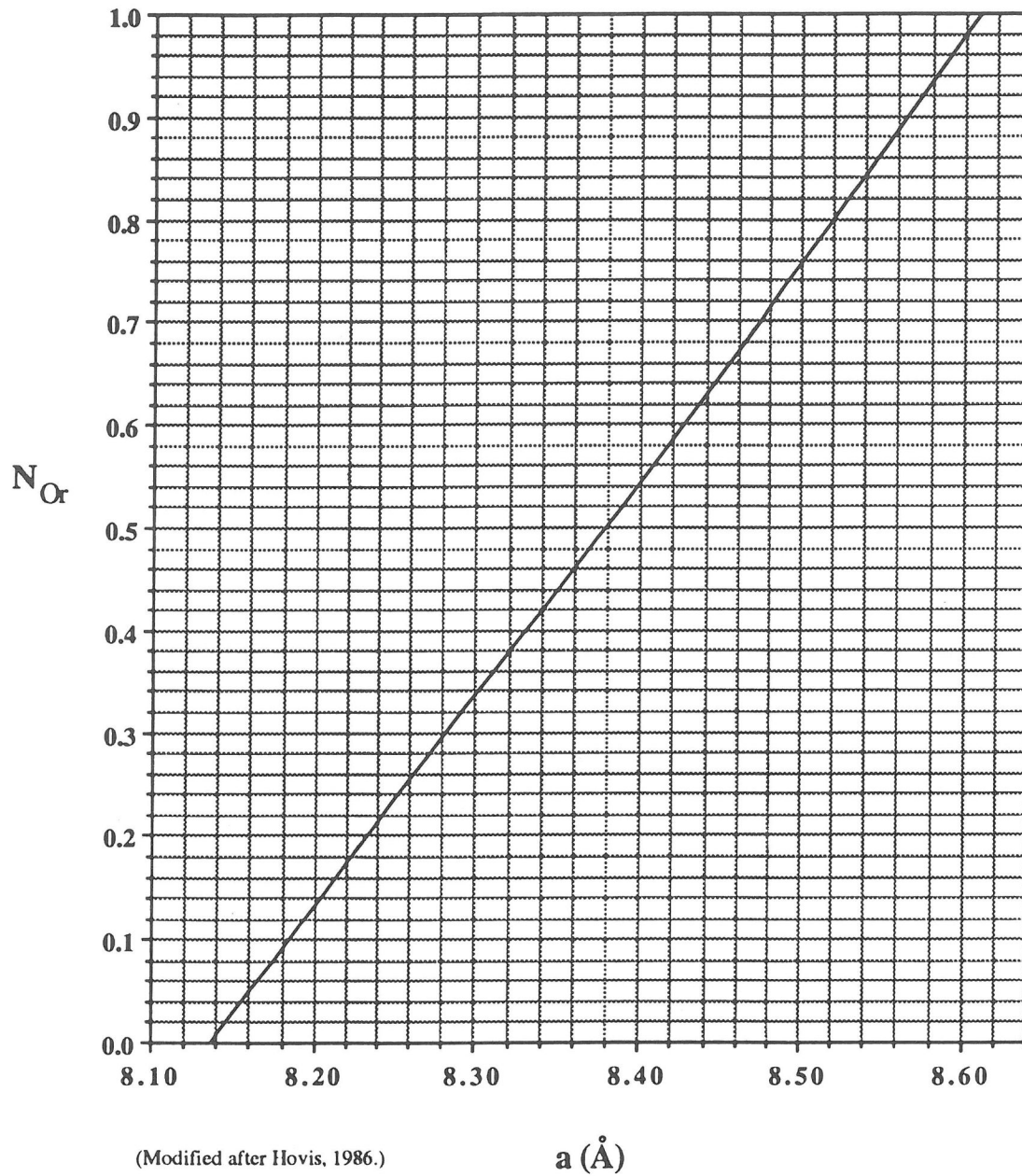
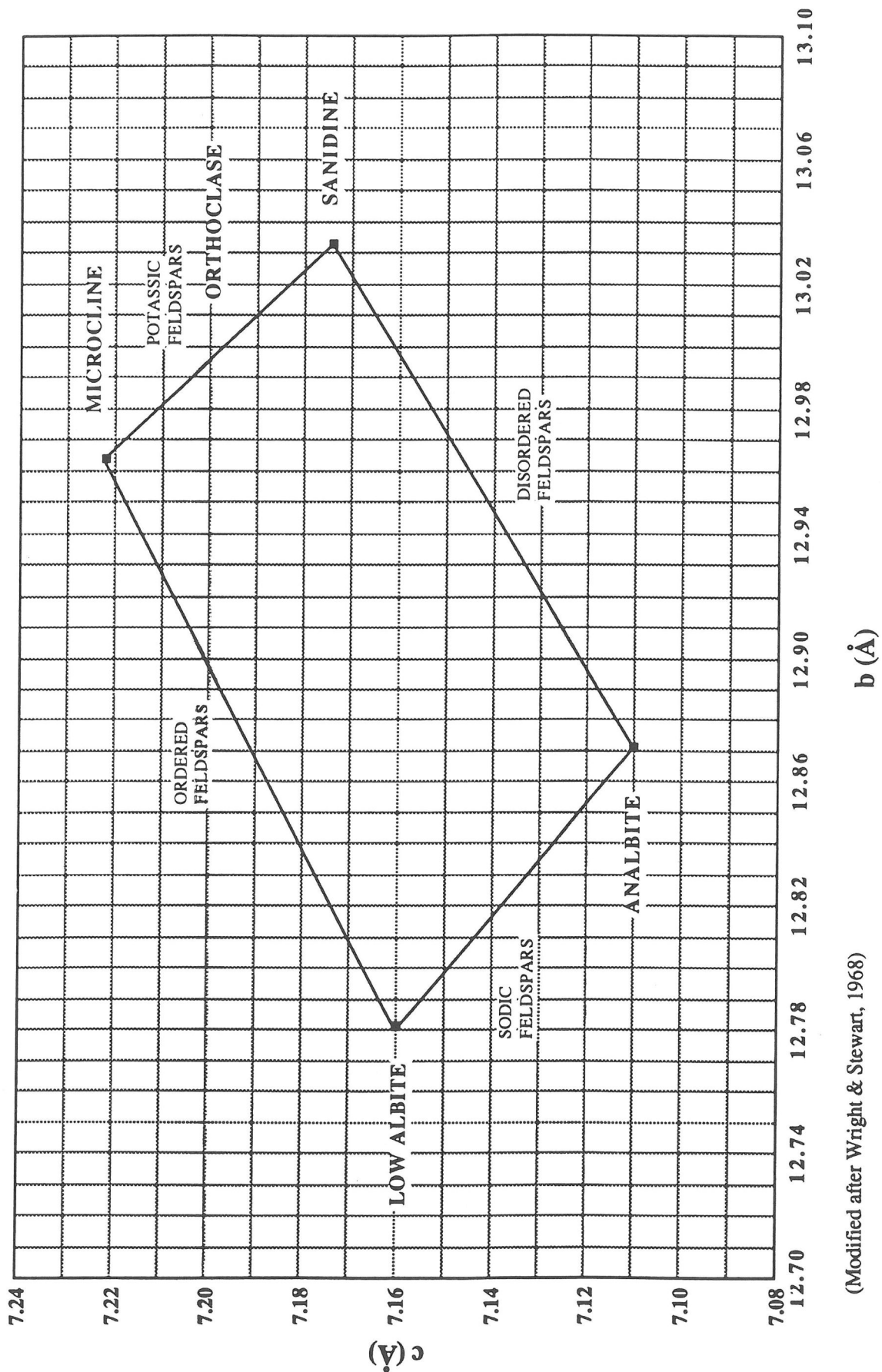


FIGURE 1. A plot of N_{Or} against the a unit-cell dimension. The a unit-cell dimension is affected to a small degree by ordering. Although slightly different curves should be used for different Al-Si distributions, the curve above [Eqn. (5)] is an “average” relationship that does not take state of ordering into account.

FIGURE 2



(Modified after Wright & Stewart, 1968)

(Fig. 2; similar to Wright and Stewart, 1968, and Kroll and Ribbe, 1983) illustrates this point well; note, for example, the changes of \bar{b} and \bar{c} for pure-K feldspars in the conversion of orthoclase (relatively ordered) to sanidine (disordered).

You will see from Figure 2 that \bar{b} and \bar{c} also are affected by composition; both parameters expand with increased potassium content in the feldspar. Because \bar{b} and \bar{c} are functions of both ordering and composition, neither can be used alone to determine either the state of Al-Si order or composition. Nevertheless, it is relatively easy to obtain the information we need. We shall take advantage of the fact that we now have compositional information determined in Part I.

We shall illustrate two methods that can be used to determine state of order. In Parts A-G below, the \bar{c} unit-cell dimension alone is utilized. In Part A we “subtract out” the effects of composition on the observed value of \bar{c} (\bar{c}_{obs}). This is done by taking \bar{c}_{obs} of your sodium-bearing feldspar and sliding it along an “iso-order” line in Figure 3 to the pure-potassium end of a K-Na “ion-exchange series.” The resulting parameter, \bar{c}_K , is the \bar{c} -value that your feldspar would have had if it had contained no sodium.

- A. To compute \bar{c}_K , use Eqn. (6) below (Hovis, 1986). Employ the \bar{c} unit-cell value determined from your X-ray data (\bar{c}_{obs}) and the N_{Or} from Part IB above.

$$\bar{c}_K = \bar{c}_{\text{obs}} + 0.038 (1 - N_{\text{Or}}) \quad \text{Eqn. (6)}$$

- B. Since \bar{c}_K is sensitive to Al-Si distribution (see Fig. 4), it may be used to determine Z. The equation below (Hovis, 1986) expresses the line on Figure 4 that relates these two parameters. Calculate Z using the \bar{c}_K from Part A above.

$$Z = -144.962 + 20.2032 \bar{c}_K \quad \text{Eqn. (7)}$$

- C. Next compute $N_{\text{Al(T1)}}$ and $N_{\text{Al(T2)}}$ using Eqns. (8) and (9) below (Hovis, 1986).

$$N_{\text{Al(T1)}} = (1 + Z) / 4 = -34.3939 + 4.82884 \bar{c}_K \quad \text{Eqn. (8)}$$

$$N_{\text{Al(T2)}} = (1 - Z) / 4 = +34.8939 - 4.82884 \bar{c}_K \quad \text{Eqn. (9)}$$

[As a check on your calculations, note that for any monoclinic K-Na feldspar $N_{\text{Al(T1)}}$ and $N_{\text{Al(T2)}}$ should sum to 0.50.]

- D. $N_{\text{Si(T1)}}$ and $N_{\text{Si(T2)}}$, the mole fractions of Si in T1 and T2, also may be computed. This is very simple, because the mole fractions of Al and Si add to 1.0 in each site. Thus:

$$N_{\text{Si(T1)}} = 1 - N_{\text{Al(T1)}} \quad \text{Eqn. (10)}$$

$$N_{\text{Si(T2)}} = 1 - N_{\text{Al(T2)}} \quad \text{Eqn. (11)}$$

- E. Given the fact that natural and synthetic feldspars have Z-values ranging from about 0.8 (most ordered) to 0.07 (most disordered), rank the state of order of your feldspar:

Highly ordered? Highly disordered? In between?

- F. Using Figure 5 (Hovis, unpublished), employ the Z-value of your feldspar to approximate the temperature at which it equilibrated.

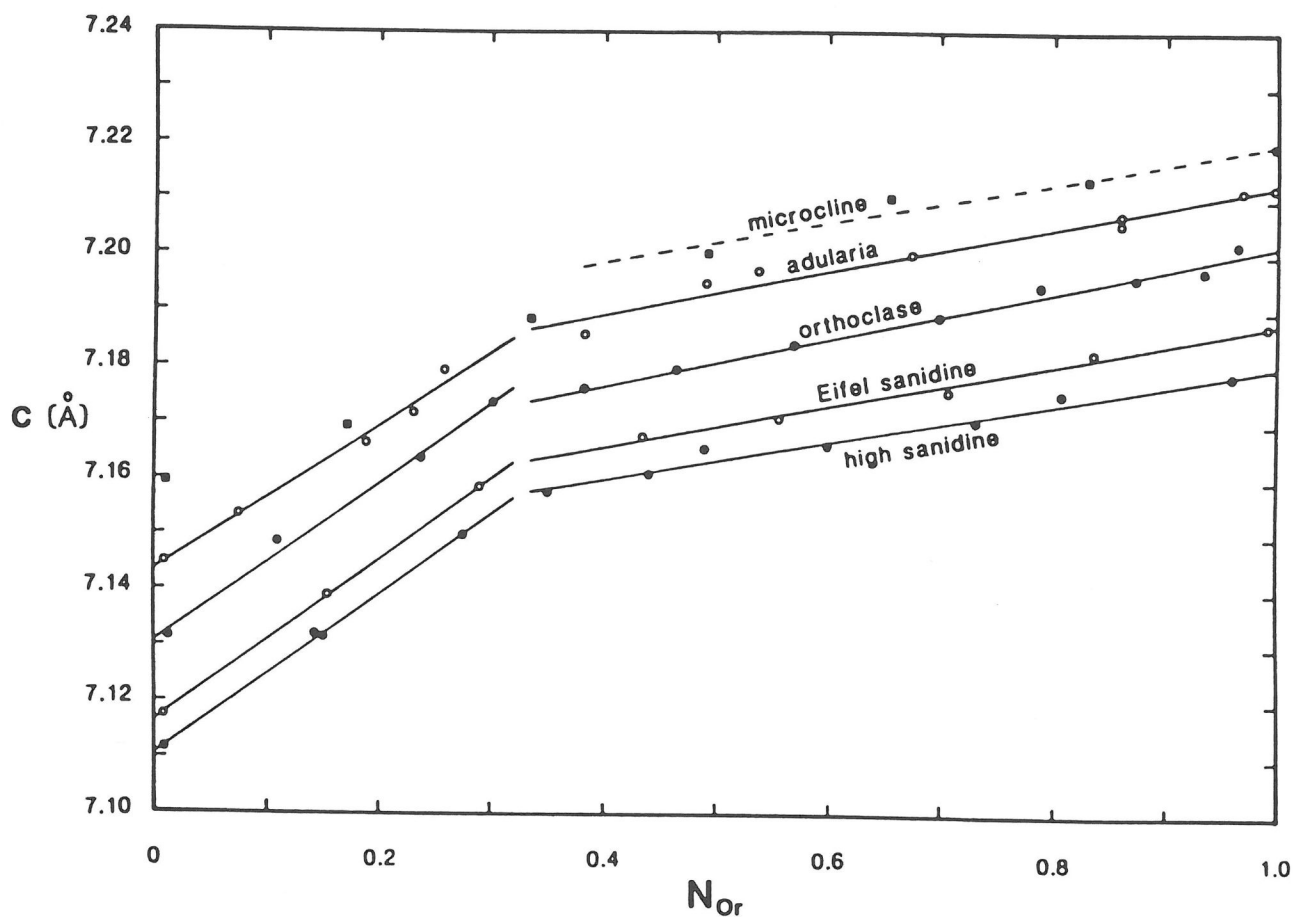


FIGURE 3. The c unit-cell dimension plotted against N_{Or} for several iso-structural series of alkali feldspars (Hovis, 1986). Note that c is a function of both chemical composition and Al-Si distribution. One can "correct" the observed c -value of an alkali feldspar for Na by sliding it along a line of "constant Al-Si order" (e.g., the "adularia," "orthoclase," or "sanidine" lines) to the pure-K end of a series ($N_{Or} = 1$). This produces the value c_K , which is the c -value for the pure potassium end member of the series. Such a feldspar would have the same Al-Si distribution as its Na-bearing analog.

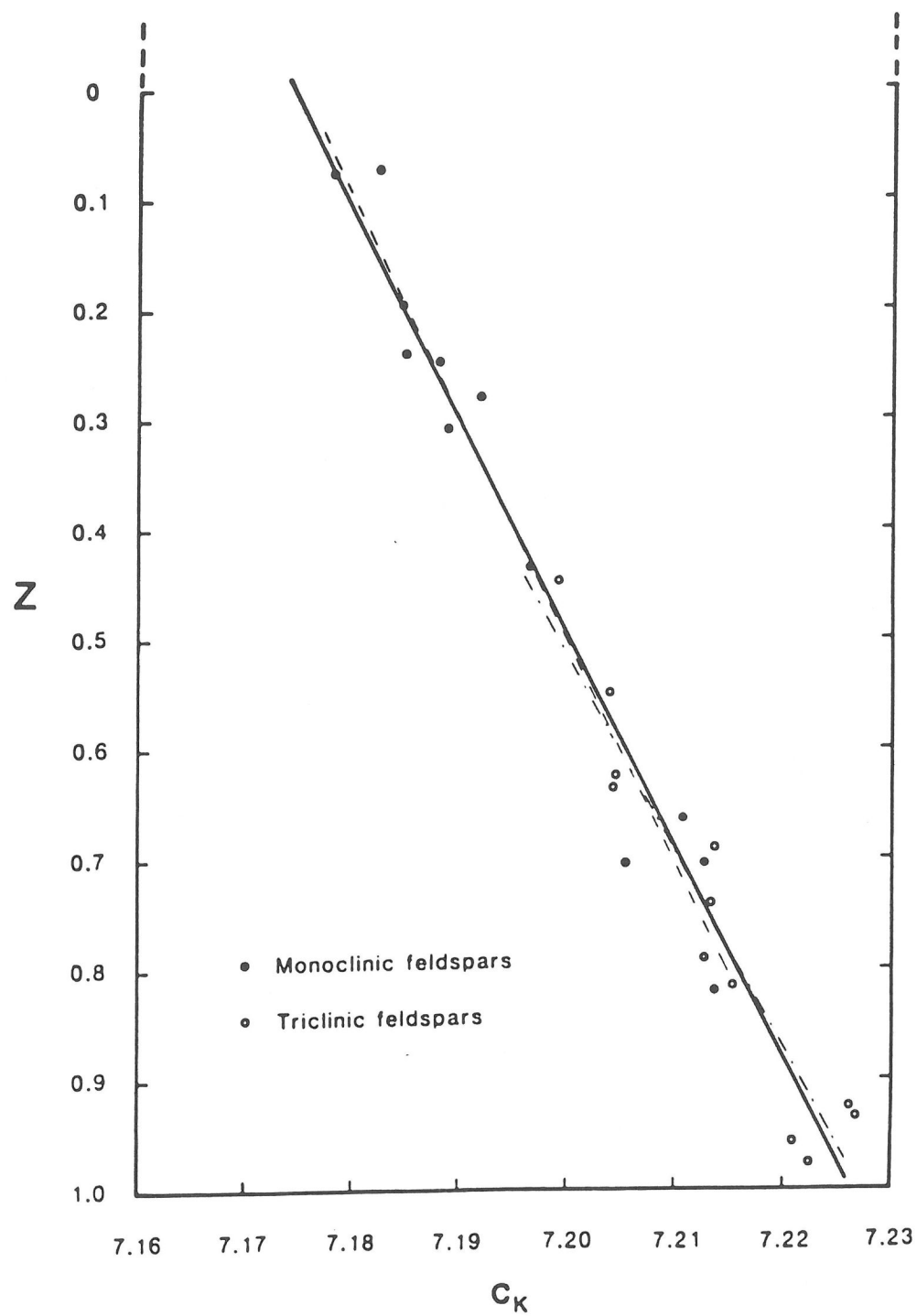


FIGURE 4. Plot of Z against c_K for alkali feldspars having various degrees of order (Hovis, 1986). Separate (light dashed) lines represent data for feldspars with triclinic and monoclinic Al-Si distributions; however, these have virtually the same slope. The heavy line is based on data for all feldspars and is expressed by Eqn. (7).

- G. Is it more likely that your alkali feldspar came from a (a) hydrothermal vein, (b) pegmatite, or (c) high-temperature lava?

Research on the use of unit-cell dimensions to estimate Al-Si distribution in alkali feldspars has been pioneered by a number of workers, including Wright and Stewart (1968), Stewart and Ribbe (1969), and Kroll and Ribbe (1983). A commonly used method for simultaneously estimating both the composition and state of order of an alkali feldspar is to plot its c unit-cell dimension (that is, c_{obs}) against its b dimension:

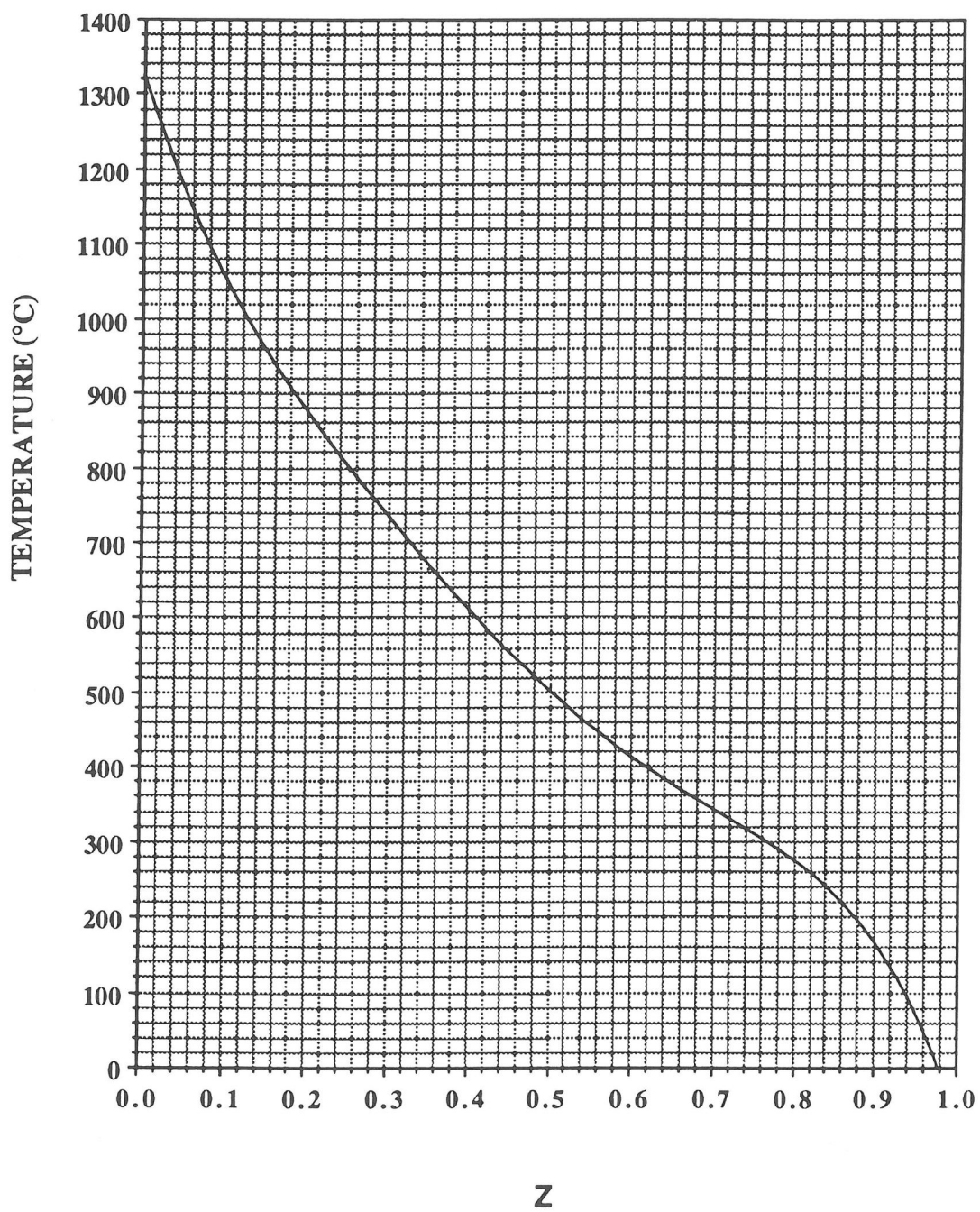
- H. Plot on Figure 2 the b versus the c (c_{obs}) unit-cell dimension of your feldspar.
- I. Does the position of the plotted point make sense for the N_{Or} and Al-Si distribution computed above for your feldspar? Briefly discuss.

PART III: MOLAR VOLUME AND DENSITY DETERMINATION

Volume and density are important properties of minerals and rocks. Molar volume, the space occupied by one "mole" of a substance, relates closely to the conditions of stability of a mineral; as pressure increases with depth in the Earth, materials that occupy less volume are favored. Density too is a fundamental property of any material and an important parameter to which geophysicists relate both gravity and seismic data. It is density differences among materials that help geologists interpret the structure and composition of rocks that exist below the Earth's surface. The molar volume of a mineral can be determined directly from X-ray data, and with accompanying chemical information density also can be estimated.

The output from the unit-cell dimension calculations should include information on unit-cell volume, that is, the volume occupied by one unit cell of your feldspar. Since there are four formula units in each unit cell, you can easily compute how much volume one formula unit takes up. If you multiply the latter number by Avogadro's constant (6.022×10^{23}), you would know how much volume one mole of your feldspar occupies (molar volume). All that remains, then, is to convert volume in \AA^3 to volume in more familiar units of cm^3 (a conversion factor of 10^{-24}). All these conversions can be accomplished simultaneously by multiplying unit-cell volume by 0.15055. Then, once you know molar volume, you can take advantage of chemical information to compute density. Just follow the instructions below.

- A. Multiply the unit-cell volume ($\text{\AA}^3/\text{unit cell}$) by 0.15055 to convert to molar volume in cm^3/mole .
- B. Write out the chemical formula determined in Part IB above, based upon eight oxygens. Now take the atomic weights of chemical elements in the formula (K, Na, Al, Si, and O) and multiply each by the relevant subscript, then add the resulting five numbers. This sum is the gram formula weight, that is the weight of one mole, of your feldspar.
- C. You now know both the volume (Part A) and the weight (Part B) of one mole of your feldspar. In order to compute its density, simply divide the gram formula weight (g/mole) by the molar volume (cm^3/mole). Note that the resulting units will be in g/cm^3 .



[This graph will produce approximate temperatures; it is still in a developmental stage (Hovis, unpublished).]

FIGURE 5. Temperature plotted against Z for alkali feldspars having various degrees of order.

- D. Check the density (or specific gravity) of alkali feldspar (or microcline, orthoclase, or sanidine) in an appropriate reference book, such as your Mineralogy textbook. What value is given?

How does your value compare? [It should be close; if it isn't, check your calculations.]

- E. How does the density of an alkali feldspar compare to those of minerals such as forsterite (olivine), enstatite (pyroxene), and pyrope (garnet)?
- F. Based on the comparison made in Part E, would you expect alkali feldspars to be more abundant in the Earth's crust or the Earth's mantle?

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NOTES TO THE INSTRUCTOR

1. It is important that the feldspar you give each student is monoclinic. To differentiate orthoclase and sanidine (monoclinic) from microcline (triclinic), compare X-ray data between 18° and 35° 2θ (CuK_α radiation) using Borg and Smith (1969) or other data.
2. It also is important to give students single-phase specimens. To identify perthitic samples, look at the (201) peak; for two-phase specimens the latter will be double, or very broad.
3. The best material for highly ordered K-feldspar is probably “adularia,” such as the Swiss vein deposits. Be careful, though, in some cases these are triclinic.

Single-phase intermediately-ordered orthoclase can be hard to find, because in plutonic (including pegmatitic) environments it often re-equilibrates to microcline during cooling. The Benson pegmatite in New York provides good material, and the yellowish or greenish orthoclases from Madagascar pegmatites are excellent. As highly potassic materials, these feldspars beat mother nature by hitting the solvus at a temperature that was too low for exsolution to occur.

Highly disordered sanidine can be obtained from phenocrysts in lavas, or you can synthesize it yourself by cooking K-rich feldspar at 1050°C for about three weeks.

4. If your X-ray system is out of alignment, the resulting unit-cell dimensions will be in error. Obviously, this will adversely affect the results.
5. In addition to (or in place of) the equations given, you also can have your students graphically determine parameters such as N_{Or} , c_K , and Z from the figures.
6. Obviously, this exercise is fairly sophisticated. However, my students have done well with it. One place you might have to help them is with inspection of the X-ray data once the unit-cell dimensions have been calculated, showing them what to look for in the way of mistakes. If in calculating unit-cell dimensions a student has made a mistake in typing a 2θ value (e.g., 21.148° instead of 20.148°), or in indexing a peak, it is likely to have very significant consequences on the results. So, it would be good to check on quality somewhere along the line, or to give students an idea of how to identify mistakes, e.g., by looking at “residuals” (calculated versus observed peak positions), or by inspecting the magnitudes of the “standard errors” that the calculations produce).
7. Remember that some feldspars re-equilibrate as they cool, especially in slow-cooling environments. Therefore, I have been careful to communicate the concept that Al-Si distribution represents the temperature of “equilibration” as opposed to the temperature of “formation.”

DETERMINATION OF CHEMICAL COMPOSITION, STATE OF ORDER, MOLAR VOLUME, AND DENSITY OF A MONOCLINIC ALKALI FELDSPAR USING X-RAY DIFFRACTION

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INTRODUCTION

Alkali feldspars (commonly referred to as “potassium feldspars”) are among the most abundant minerals in the Earth’s crust. As such, they have the potential to provide important information about the rocks in which they occur. Using X-ray data, it is possible to characterize both the chemical composition and state of order of an alkali feldspar, and in some instances to approximate the temperature at which the feldspar equilibrated. Molar volume and density, fundamental properties of any mineral, also can be determined.

Although many chemical substitutions occur in these minerals, the replacement of K by Na is the most common. Thus, as a first approximation, alkali feldspars can be thought of as solid solutions varying from potassium-rich to sodium-rich end members, that is, from KAlSi_3O_8 to $\text{NaAlSi}_3\text{O}_8$. Mineralogists characterize alkali feldspar composition by a parameter called N_{Or} , which is simply the “mole fraction” of potassium in the mineral. If $N_{\text{Or}} = 0.7$, for example, a formula of $\text{K}_{0.7}\text{Na}_{0.3}\text{AlSi}_3\text{O}_8$ is implied (note that Na and K always add to 1.0). Both the a unit-cell dimension and the (201) X-ray diffraction peak of an alkali feldspar are quite sensitive to K:Na ratio. In this exercise both will be used to estimate the composition of an alkali feldspar.

In addition to chemical composition, alkali feldspars are characterized by their state of “order” or “disorder.” Ordering phenomena can occur in any crystalline material in which two or more ions compete for symmetrically nonequivalent crystallographic sites. In monoclinic alkali feldspars it is aluminum (Al) and silicon (Si) ions that occupy both of the crystallographically distinct tetrahedral sites (named T1 and T2; see Fig. 2 of Hovis, this publication). Ordering relationships, however, are found in many other mineral series, including pyroxenes, amphiboles, and micas, and in sites other than tetrahedral ones. Because these relationships are temperature- and/or pressure-dependent, they can give important information about the conditions under which a mineral has equilibrated.

The state of order in monoclinic alkali feldspars is defined by the distribution of Al and Si between the two tetrahedral sites. To illustrate, let us suppose that there are a total of 2000 tetrahedra in a tiny feldspar crystal. Since there are equal numbers of T1 and T2 sites, 1000 of these would be T1 sites and 1000 would be T2 sites. Because of the 1:3 Al:Si ratio, 500 Al ions and 1500 Si ions would occupy these sites. The most “ordered” possible monoclinic feldspar crystal would have all 500 Al ions in one site (the T1). The 1500 Si ions would fill the remaining 500 T1 sites and all 1000 of the T2 sites. Thus, the fraction of Al ions in the T1 site (symbolized $N_{\text{Al(T1)}}$) of such a crystal would be 0.50 (500/1000), and the fraction of Al in T2 ($N_{\text{Al(T2)}}$) would be 0.00. On the other hand, a “perfectly disordered” crystal would have a “random” distribution of Al and Si between the two sites (that is, the same occupancy in both sites). In such a case, 250 Al

ions and 750 Si ions would fill each site. In this case, $N_{\text{Al(T1)}} = N_{\text{Al(T2)}} = 0.25$ (250/1000).

A convenient way to express the Al-Si distribution of an alkali feldspar is with a single parameter, Z , defined as twice the difference of the atom mole fractions of Al in the two tetrahedral sites (Thompson, 1969 and 1970):

$$Z = 2 [N_{\text{Al(T1)}} - N_{\text{Al(T2)}}] \quad \text{Eqn. (1)}$$

Substituting into this equation the above mole fractions of Al, we see that a perfectly ordered monoclinic feldspar would have a Z -value of 1.0 (2 times 0.50), whereas a perfectly disordered one would have a value of 0.0 (2 times zero). Although we can relate the Z -values of any natural sample to this range (samples with Z -values closer to 1.0 being more ordered, and those closer to 0.0 more disordered), bear in mind that naturally occurring alkali feldspars seem to possess Z -values in a range from about 0.8 to 0.2; even synthetically disordered ones have Z -values of only 0.07 or so (Hovis, 1986). We can use X-ray data to estimate the Z -value of any monoclinic alkali feldspar.

Just as Z can be calculated from site populations, site populations can be calculated from Z . Considering Eqn. (1) above, and the fact that $N_{\text{Al(T1)}} + N_{\text{Al(T2)}}$ must sum to 0.5 in the simple K-Na alkali feldspar system, one can use these two simultaneous equations to demonstrate that

$$N_{\text{Al(T1)}} = (1 + Z) / 4 \quad \text{Eqn. (2)}$$

$$N_{\text{Al(T2)}} = (1 - Z) / 4 \quad \text{Eqn. (3)}$$

So, just as site populations can be used to calculate Z , Z -values can be converted to the fractions of aluminum (and silicon) in each of the tetrahedral sites. Whether one chooses a Z -value or the individual site populations to express the state of order is arbitrary; the two are equivalent.

For alkali feldspars, the state of order is almost solely dependent on the temperature of equilibration, ordered samples having equilibrated at lower temperatures (e.g., hydrothermal veins) than disordered ones (e.g., volcanic phenocrysts). Because geologists are interested in the conditions to which a rock has been exposed, the temperature information that a feldspar-bearing rock might provide is potentially valuable. One must remember, however, that feldspars can re-equilibrate (become more ordered) as they cool; the environments most likely to have preserved temperature information are either those in which cooling occurred rapidly under relatively dry conditions, or ones in which temperatures never were very high.

DATA COLLECTION

Each student should obtain a monoclinic alkali feldspar from the instructor and prepare the sample for X-ray analysis. If students have been instructed on the use of an "internal standard" (silicon makes a good one), include it in the sample, otherwise ignore the internal standard. If you do not use an internal standard, however, your X-ray system must be relatively well aligned, because errors in 2θ will produce errors in both peak positions and unit-cell dimensions.

1. If using $\text{CuK}\alpha$ radiation, collect X-ray data from 18° to 60° 2θ . If using another type of radiation, adjust these values appropriately. If using a diffractometer, a scan rate of $1^\circ/\text{min}$ produces better data, but rates up to $5^\circ/\text{min}$ may be employed.

2. Measure and record the positions and intensities of as many peaks/lines as possible. If an internal standard was mixed with the sample, correct all peak positions using data from the standard.
3. Identify the Miller Indices of each peak/line. The data in Borg and Smith (1969) for adularia, orthoclase, and sanidine will be helpful. If you cannot determine which of the latter data sets is most closely comparable to yours, index peaks using the data for orthoclase. Peaks also can be indexed using information in the JCPDS data base.
4. Using a lattice constant refinement program such as LCLSQ (Burnham, 1962), or the "electronic spreadsheet" of Novak and Colville (1989) or software included with an automated X-ray system, compute the unit-cell dimensions of your sample. In making this calculation, you should ignore "overlapping" peaks/lines (i.e., those for which there is more than one set of Miller Indices) should be ignored. Remember to refine the unit-cell dimensions in the monoclinic crystal system.
5. Record the position of the ($\bar{2}01$) peak, found in the general vicinity of $21^\circ 2\theta$ for $\text{CuK}\alpha$ radiation.

PART I: COMPOSITION DETERMINATION

Remember that the principal chemical substitution in alkali feldspars is $\text{K} = \text{Na}$. As larger potassium ions replace smaller sodium ions, the interplanar spacings (d_{hkl}) generally increase, and as a result all three of the unit-cell axes (a , b , c) expand. Of these a is the most sensitive to composition (Fig. 1). Furthermore, as any one interplanar spacing increases, the corresponding 2θ decreases (a function of the Bragg equation). As an individual peak/line, the ($\bar{2}01$) is especially sensitive to $\text{K} = \text{Na}$ substitution, changing from about $22^\circ 2\theta$ for pure-Na feldspar to 21° for pure-K feldspar ($\text{CuK}\alpha$ radiation; see Fig. 3 of Hovis, this publication).

- A. Use the ($\bar{2}01$) peak of your feldspar and the equation below (Hovis, 1989) to compute N_{Or} . (Values of 2θ should be for $\text{CuK}\alpha$ radiation.)

$$N_{\text{Or}} = 70.726 - 5.6200 (2\theta) + 0.10936 (2\theta)^2 \quad \text{Eqn. (4)}$$

- B. Substitute the a unit-cell dimension of your feldspar into the equation below (Hovis, 1986) as a second method of computing N_{Or} ; this should produce a value similar to that in Part A.

$$N_{\text{Or}} = -366.3261 + 129.2335 a - 15.42053 a^2 + 0.6232109 a^3 \quad \text{Eqn. (5)}$$

- C. The two methods will not compare perfectly, but they should be close. How well do the two N_{Or} values agree?
- D. If they do not agree well, what might be the reason(s)?

PART II: DETERMINATION OF STATE OF ORDER

Just as with composition, peak positions and unit-cell dimensions are affected by the interchange of Al and Si ions between T1 and T2 tetrahedral sites. At any one composition, disorder causes the c dimension to shorten and the b dimension to lengthen. A plot of c against b

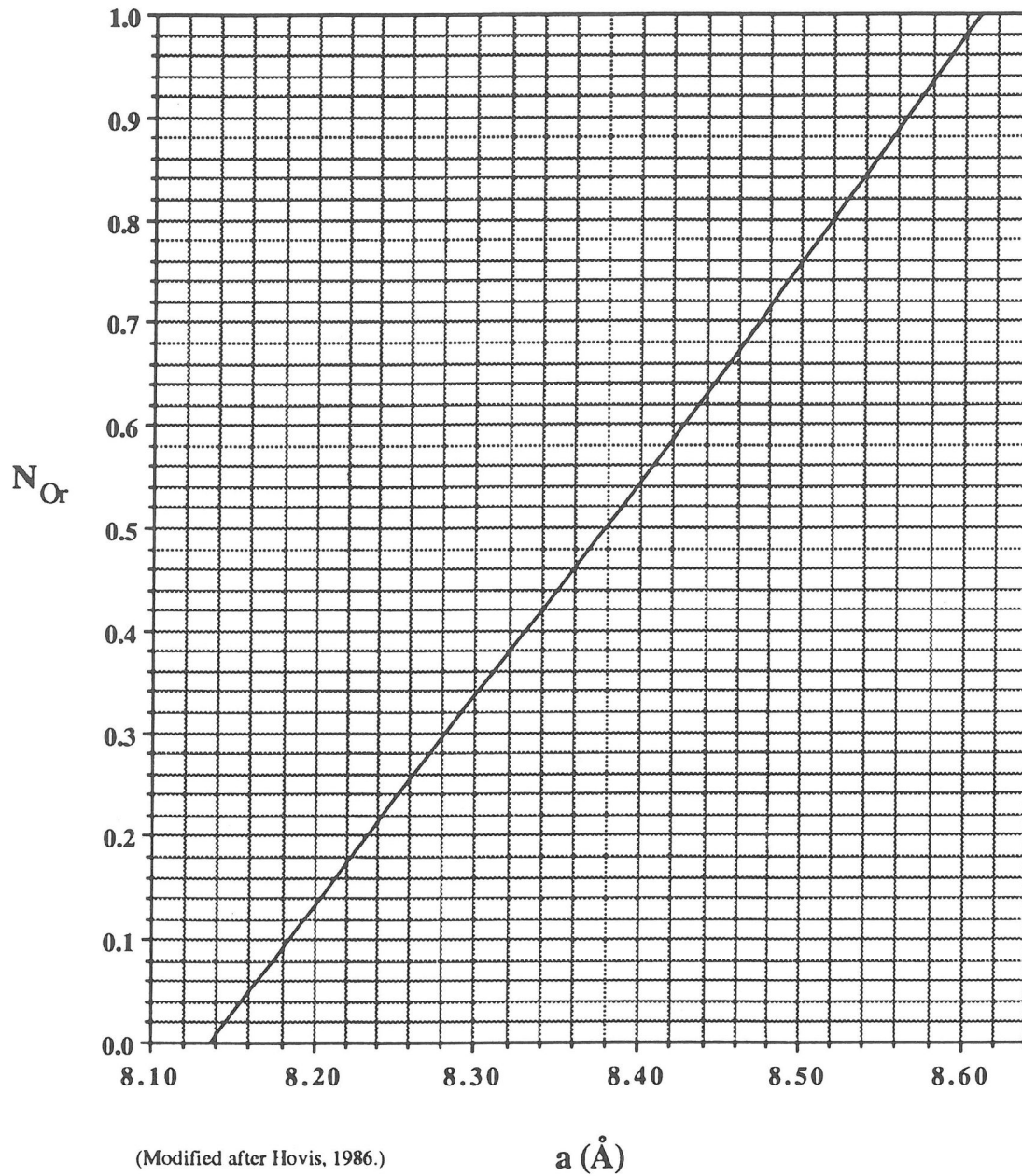
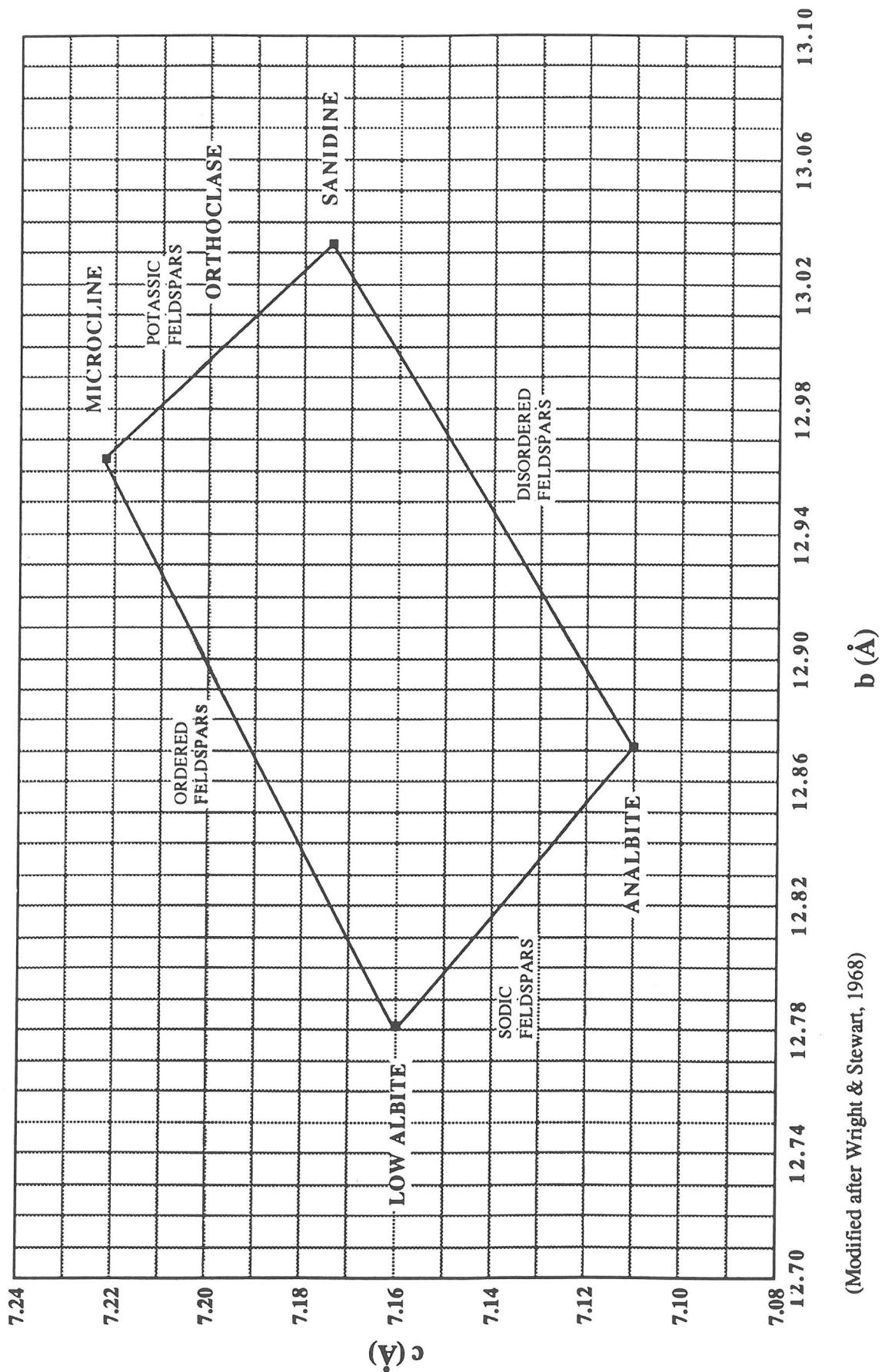


FIGURE 1. A plot of N_{Or} against the a unit-cell dimension. The a unit-cell dimension is affected to a small degree by ordering. Although slightly different curves should be used for different Al-Si distributions, the curve above [Eqn. (5)] is an “average” relationship that does not take state of ordering into account.

FIGURE 2



(Modified after Wright & Stewart, 1968)

(Fig. 2; similar to Wright and Stewart, 1968, and Kroll and Ribbe, 1983) illustrates this point well; note, for example, the changes of \bar{b} and \bar{c} for pure-K feldspars in the conversion of orthoclase (relatively ordered) to sanidine (disordered).

You will see from Figure 2 that \bar{b} and \bar{c} also are affected by composition; both parameters expand with increased potassium content in the feldspar. Because \bar{b} and \bar{c} are functions of both ordering and composition, neither can be used alone to determine either the state of Al-Si order or composition. Nevertheless, it is relatively easy to obtain the information we need. We shall take advantage of the fact that we now have compositional information determined in Part I.

We shall illustrate two methods that can be used to determine state of order. In Parts A-G below, the \bar{c} unit-cell dimension alone is utilized. In Part A we “subtract out” the effects of composition on the observed value of \bar{c} (\bar{c}_{obs}). This is done by taking \bar{c}_{obs} of your sodium-bearing feldspar and sliding it along an “iso-order” line in Figure 3 to the pure-potassium end of a K-Na “ion-exchange series.” The resulting parameter, \bar{c}_K , is the \bar{c} -value that your feldspar would have had if it had contained no sodium.

- A. To compute \bar{c}_K , use Eqn. (6) below (Hovis, 1986). Employ the \bar{c} unit-cell value determined from your X-ray data (\bar{c}_{obs}) and the N_{Or} from Part IB above.

$$\bar{c}_K = \bar{c}_{\text{obs}} + 0.038 (1 - N_{\text{Or}}) \quad \text{Eqn. (6)}$$

- B. Since \bar{c}_K is sensitive to Al-Si distribution (see Fig. 4), it may be used to determine Z. The equation below (Hovis, 1986) expresses the line on Figure 4 that relates these two parameters. Calculate Z using the \bar{c}_K from Part A above.

$$Z = -144.962 + 20.2032 \bar{c}_K \quad \text{Eqn. (7)}$$

- C. Next compute $N_{\text{Al(T1)}}$ and $N_{\text{Al(T2)}}$ using Eqns. (8) and (9) below (Hovis, 1986).

$$N_{\text{Al(T1)}} = (1 + Z) / 4 = -34.3939 + 4.82884 \bar{c}_K \quad \text{Eqn. (8)}$$

$$N_{\text{Al(T2)}} = (1 - Z) / 4 = +34.8939 - 4.82884 \bar{c}_K \quad \text{Eqn. (9)}$$

[As a check on your calculations, note that for any monoclinic K-Na feldspar $N_{\text{Al(T1)}}$ and $N_{\text{Al(T2)}}$ should sum to 0.50.]

- D. $N_{\text{Si(T1)}}$ and $N_{\text{Si(T2)}}$, the mole fractions of Si in T1 and T2, also may be computed. This is very simple, because the mole fractions of Al and Si add to 1.0 in each site. Thus:

$$N_{\text{Si(T1)}} = 1 - N_{\text{Al(T1)}} \quad \text{Eqn. (10)}$$

$$N_{\text{Si(T2)}} = 1 - N_{\text{Al(T2)}} \quad \text{Eqn. (11)}$$

- E. Given the fact that natural and synthetic feldspars have Z-values ranging from about 0.8 (most ordered) to 0.07 (most disordered), rank the state of order of your feldspar:

Highly ordered? Highly disordered? In between?

- F. Using Figure 5 (Hovis, unpublished), employ the Z-value of your feldspar to approximate the temperature at which it equilibrated.

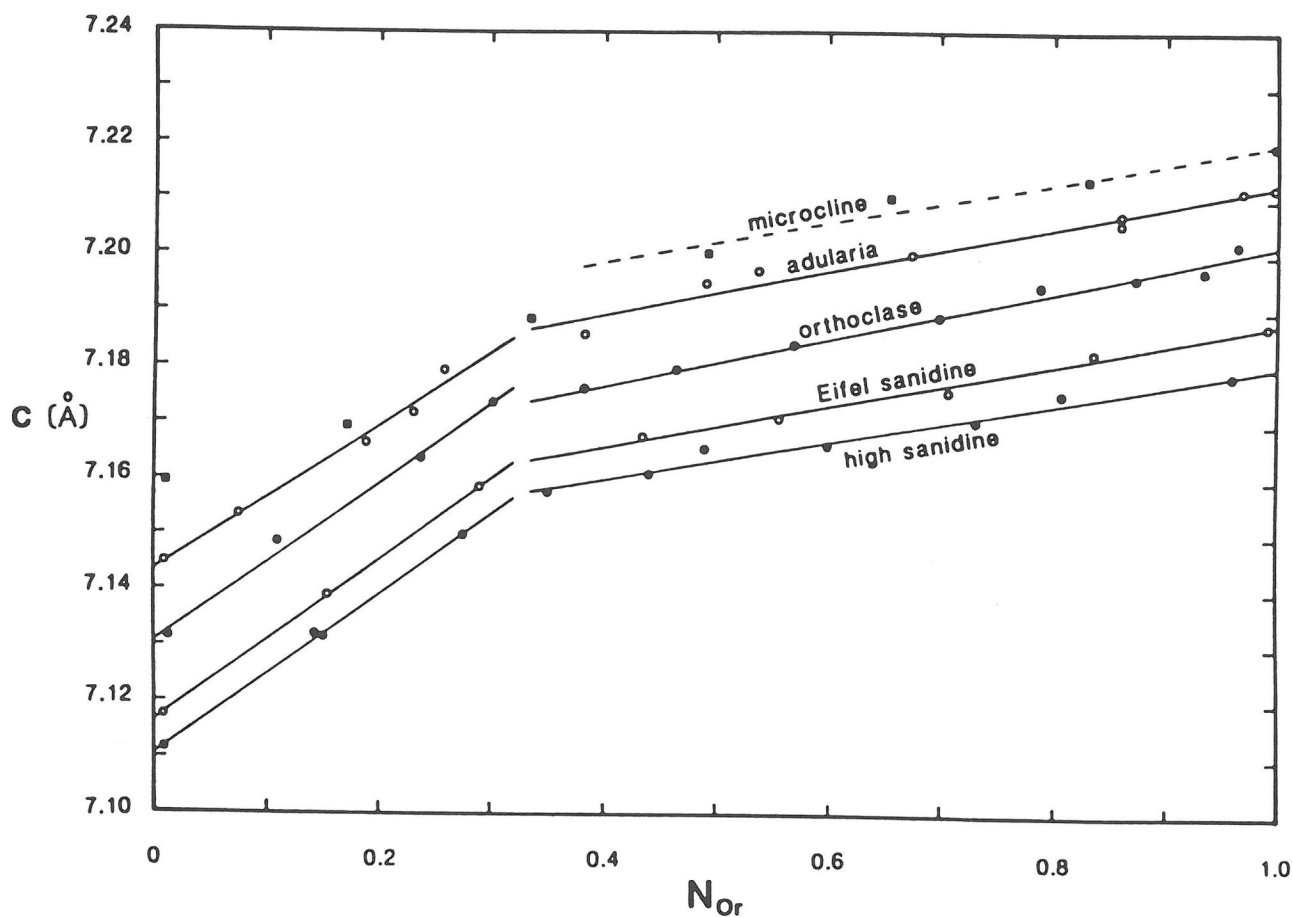


FIGURE 3. The c unit-cell dimension plotted against N_{Or} for several iso-structural series of alkali feldspars (Hovis, 1986). Note that c is a function of both chemical composition and Al-Si distribution. One can "correct" the observed c -value of an alkali feldspar for Na by sliding it along a line of "constant Al-Si order" (e.g., the "adularia," "orthoclase," or "sanidine" lines) to the pure-K end of a series ($N_{Or} = 1$). This produces the value c_K , which is the c -value for the pure potassium end member of the series. Such a feldspar would have the same Al-Si distribution as its Na-bearing analog.

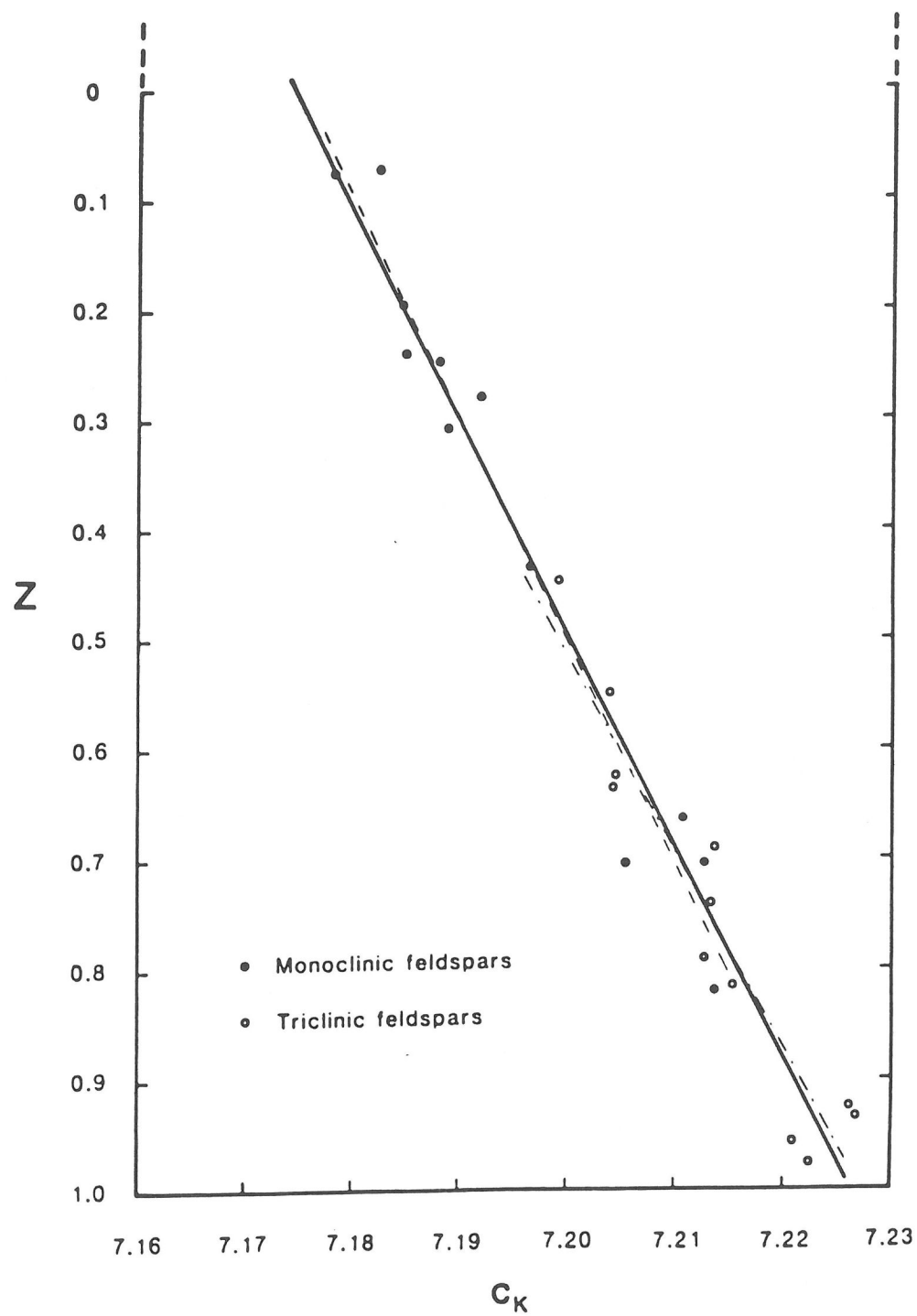


FIGURE 4. Plot of Z against c_K for alkali feldspars having various degrees of order (Hovis, 1986). Separate (light dashed) lines represent data for feldspars with triclinic and monoclinic Al-Si distributions; however, these have virtually the same slope. The heavy line is based on data for all feldspars and is expressed by Eqn. (7).

- G. Is it more likely that your alkali feldspar came from a (a) hydrothermal vein, (b) pegmatite, or (c) high-temperature lava?

Research on the use of unit-cell dimensions to estimate Al-Si distribution in alkali feldspars has been pioneered by a number of workers, including Wright and Stewart (1968), Stewart and Ribbe (1969), and Kroll and Ribbe (1983). A commonly used method for simultaneously estimating both the composition and state of order of an alkali feldspar is to plot its c unit-cell dimension (that is, c_{obs}) against its b dimension:

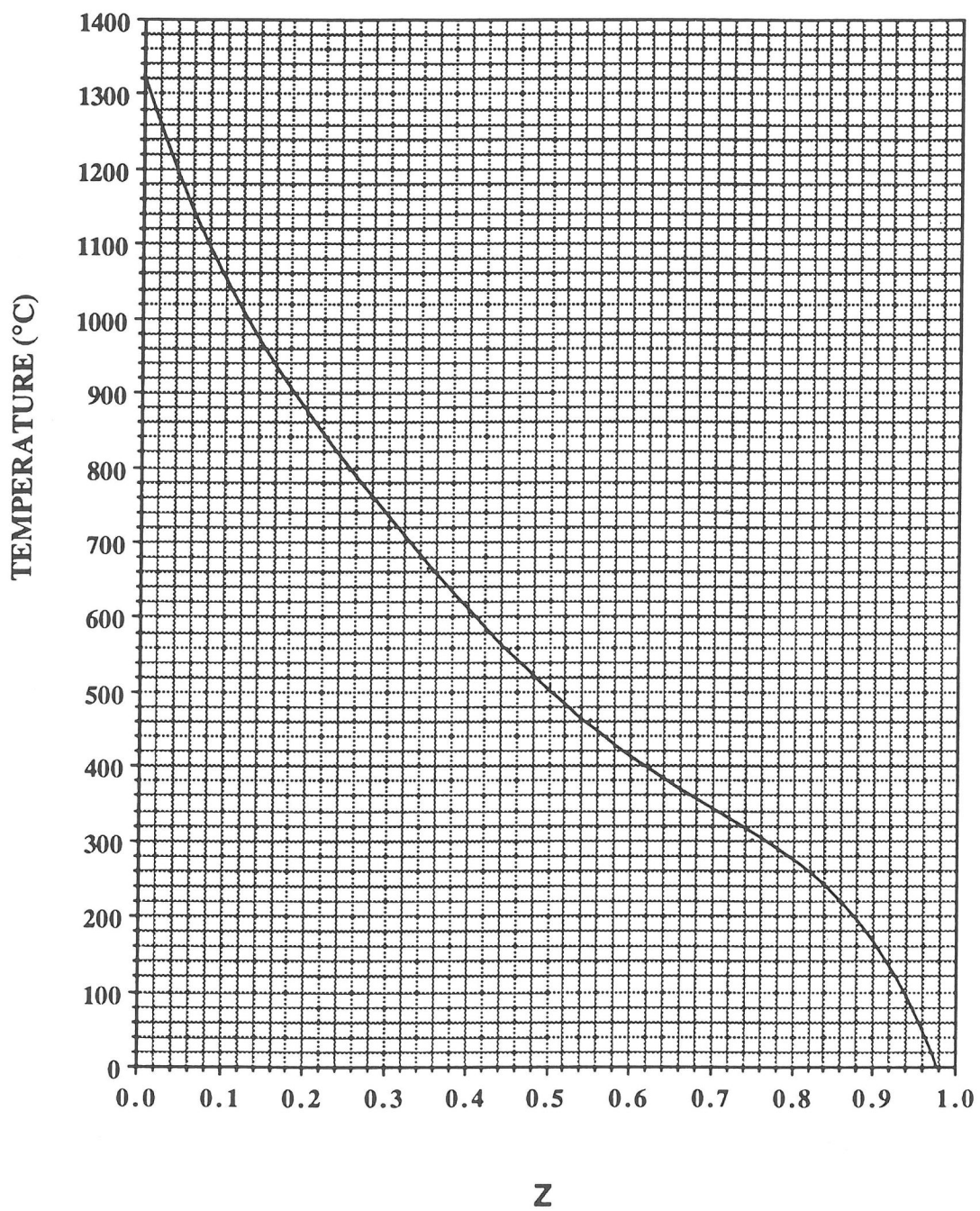
- H. Plot on Figure 2 the b versus the c (c_{obs}) unit-cell dimension of your feldspar.
- I. Does the position of the plotted point make sense for the N_{Or} and Al-Si distribution computed above for your feldspar? Briefly discuss.

PART III: MOLAR VOLUME AND DENSITY DETERMINATION

Volume and density are important properties of minerals and rocks. Molar volume, the space occupied by one "mole" of a substance, relates closely to the conditions of stability of a mineral; as pressure increases with depth in the Earth, materials that occupy less volume are favored. Density too is a fundamental property of any material and an important parameter to which geophysicists relate both gravity and seismic data. It is density differences among materials that help geologists interpret the structure and composition of rocks that exist below the Earth's surface. The molar volume of a mineral can be determined directly from X-ray data, and with accompanying chemical information density also can be estimated.

The output from the unit-cell dimension calculations should include information on unit-cell volume, that is, the volume occupied by one unit cell of your feldspar. Since there are four formula units in each unit cell, you can easily compute how much volume one formula unit takes up. If you multiply the latter number by Avogadro's constant (6.022×10^{23}), you would know how much volume one mole of your feldspar occupies (molar volume). All that remains, then, is to convert volume in \AA^3 to volume in more familiar units of cm^3 (a conversion factor of 10^{-24}). All these conversions can be accomplished simultaneously by multiplying unit-cell volume by 0.15055. Then, once you know molar volume, you can take advantage of chemical information to compute density. Just follow the instructions below.

- A. Multiply the unit-cell volume ($\text{\AA}^3/\text{unit cell}$) by 0.15055 to convert to molar volume in cm^3/mole .
- B. Write out the chemical formula determined in Part IB above, based upon eight oxygens. Now take the atomic weights of chemical elements in the formula (K, Na, Al, Si, and O) and multiply each by the relevant subscript, then add the resulting five numbers. This sum is the gram formula weight, that is the weight of one mole, of your feldspar.
- C. You now know both the volume (Part A) and the weight (Part B) of one mole of your feldspar. In order to compute its density, simply divide the gram formula weight (g/mole) by the molar volume (cm^3/mole). Note that the resulting units will be in g/cm^3 .



[This graph will produce approximate temperatures; it is still in a developmental stage (Hovis, unpublished).]

FIGURE 5. Temperature plotted against Z for alkali feldspars having various degrees of order.

- D. Check the density (or specific gravity) of alkali feldspar (or microcline, orthoclase, or sanidine) in an appropriate reference book, such as your Mineralogy textbook. What value is given?

How does your value compare? [It should be close; if it isn't, check your calculations.]

- E. How does the density of an alkali feldspar compare to those of minerals such as forsterite (olivine), enstatite (pyroxene), and pyrope (garnet)?
- F. Based on the comparison made in Part E, would you expect alkali feldspars to be more abundant in the Earth's crust or the Earth's mantle?

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NOTES TO THE INSTRUCTOR

1. It is important that the feldspar you give each student is monoclinic. To differentiate orthoclase and sanidine (monoclinic) from microcline (triclinic), compare X-ray data between 18° and 35° 2θ (CuK_α radiation) using Borg and Smith (1969) or other data.
2. It also is important to give students single-phase specimens. To identify perthitic samples, look at the (201) peak; for two-phase specimens the latter will be double, or very broad.
3. The best material for highly ordered K-feldspar is probably “adularia,” such as the Swiss vein deposits. Be careful, though, in some cases these are triclinic.

Single-phase intermediately-ordered orthoclase can be hard to find, because in plutonic (including pegmatitic) environments it often re-equilibrates to microcline during cooling. The Benson pegmatite in New York provides good material, and the yellowish or greenish orthoclases from Madagascar pegmatites are excellent. As highly potassic materials, these feldspars beat mother nature by hitting the solvus at a temperature that was too low for exsolution to occur.

Highly disordered sanidine can be obtained from phenocrysts in lavas, or you can synthesize it yourself by cooking K-rich feldspar at 1050°C for about three weeks.

4. If your X-ray system is out of alignment, the resulting unit-cell dimensions will be in error. Obviously, this will adversely affect the results.
5. In addition to (or in place of) the equations given, you also can have your students graphically determine parameters such as N_{Or} , c_K , and Z from the figures.
6. Obviously, this exercise is fairly sophisticated. However, my students have done well with it. One place you might have to help them is with inspection of the X-ray data once the unit-cell dimensions have been calculated, showing them what to look for in the way of mistakes. If in calculating unit-cell dimensions a student has made a mistake in typing a 2θ value (e.g., 21.148° instead of 20.148°), or in indexing a peak, it is likely to have very significant consequences on the results. So, it would be good to check on quality somewhere along the line, or to give students an idea of how to identify mistakes, e.g., by looking at “residuals” (calculated versus observed peak positions), or by inspecting the magnitudes of the “standard errors” that the calculations produce).
7. Remember that some feldspars re-equilibrate as they cool, especially in slow-cooling environments. Therefore, I have been careful to communicate the concept that Al-Si distribution represents the temperature of “equilibration” as opposed to the temperature of “formation.”

EXERCISES IN THE GEOCHEMICAL KINETICS OF MINERAL-WATER REACTIONS: THE RATE LAW AND RATE-DETERMINING STEP IN THE DISSOLUTION OF HALITE

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KINETICS LAB EXERCISE: DISSOLUTION OF HALITE

This lab exercise involves measuring several simple properties of halite crystals undergoing dissolution, at room temperature, and at infinite dilution. The data you generate in this lab will be used in homework exercises.

You will work in pairs, teams of two generating the data together. Divide up the labor as you see fit; what usually works best is that one team member does the experiment, the other times the runs and records the data. Make sure both team members get to perform both parts of the exercise.

LAB: For the lab, you will need: A microscope with an eyepiece scale; a wristwatch with a second hand, or equivalent; a thermometer; a micrometer to calibrate the eyepiece scale; and commercial halite (table salt).

PROCEDURE: Room temperature. Allow 2 hours.

- A. Place halite crystal on glass slide.
 - B. Measure "diameter" of the grain (length of side of cubic grain). Your instructor will provide you information on the distance between graduations on the crosshairs in your microscope's eyepiece. For greater accuracy, measure at higher magnification (e.g., 100X).
Select only grains with cross-sections as close to a perfect square as possible. Do *not* use irregularly shaped single grains, or clumps of grains.
 - C. Reduce magnification (e.g., to 40X). This makes it easier to relocate the grain once it starts dissolving. Also, make sure the cover slip is on the specimen before you add water: this makes it easier to focus.
 - D. Record the temperature of the water you are using (in °C).
 - E. Place a drop of water on the specimen. Begin timing the experiment the instant the water hits the grain. Be sure the grain is *completely* surrounded by water as quickly as possible. Having the grain located under the *center* of the cover slip will help.
 - F. Time the complete destruction of the grain, to the nearest second. Simultaneously, observe and record the changing gross morphology and surface morphology of the halite crystal.
 - G. Rinse all glassware that came into contact with the salt water (i.e., the slide, cover slip, etc.).
 - H. REPEAT AT LEAST 9-10 TIMES, USING AS WIDE RANGE OF GRAIN SIZES AS THE SAMPLE CONTAINS. Try to have at least ten trials run by the end of the lab period.
- You may want to try it a few times without timing, just to get used to (a) sample handling, (b) what the grain you're measuring looks like as it dissolves, and (c) approximately how long it takes.

PLEASE WIPE UP ALL SPILLS IMMEDIATELY!

When you are done, you should have at least ten sets of measurements of grain size, dissolution time, and temperature, for the room-temperature experiments.

PLEASE TURN OFF ALL EQUIPMENT WHEN YOU ARE FINISHED.

KINETICS PROBLEM SET: RATE LAWS FROM EXPERIMENTAL DATA I

LIST OF SYMBOLS:

C_{inf}	concentration of Na (or Cl) in the solution at infinite distance
C_{eq}	concentration of Na (or Cl) at equilibrium.
D	diffusion coefficient
D_i	tracer diffusion coefficient for species i at infinite dilution
k	rate coefficient (or decay constant)
L	characteristic length for system
N	number of parent atoms of decaying radioisotope
r	radius of the crystal at any specified t time after the start of the experiment.
r_0	radius of the crystal at the start of the experiment ($t = 0$)
t	time
t_d	time it took to dissolve the crystal with starting radius of r_0
U	advective (flow) velocity of water in system
v	molar volume of halite

1. Plot your data for r_0 vs. t (time on the horizontal [x-] axis and grain size on the vertical [y-] axis) for your room-temperature trials (use a spreadsheet or graphing program for this). (You will later plot "theoretical" curves on the same graph). Determine the slope of the "best-fit" straight line that passes closest to all the points, by either (i) using any computer program (e.g., Excel, Lotus 1-2-3, Cricket Graph, etc.) to calculate the linear least squares regression line; the program should give you the coefficients for the equation for the best-fit straight line ($y = mx + b$) to your data; or (ii) doing the same thing on your calculator (yours may even have this as a function; if not, there are formulas in some math books). Most software and calculators also provide the regression coefficient, which describes how well the regression equation fits the actual data. A "perfect" fit yields a regression coefficient of 1.0; lower values mean more deviation of the actual data from the predicted relationship.

By using a straight line to describe the kinetics, we are assuming that the reaction is zero order - that is, that the shrinkage of the grain "diameter" is constant with time - and that the rate does not depend on the composition of the solution. This is almost certainly not true, for a variety of geometric and chemical reasons. However, we did at least start with pure water (which should have no dissolved ions in it), and the geometric assumptions we made will have to do for now. If we used a much larger range of grain sizes, we might be able to observe that the best fit to the data would be some sort of curve. However, there's enough scatter in our data, and the range of values is small enough, that perhaps either a straight line or a curve could be made to fit the data. We will eventually test this idea, but for now we begin by assuming a linear relationship.

With these assumptions,

$$dr/dt = -k$$

which can be integrated between the limits $r = r_0$ @ $t = 0$ and $r = r$ @ $t = t$ (this integration is easy), giving

$$r(t) = r_0 - kt.$$

This expression is suitable for describing the radius of an individual grain at different times during its dissolution (if dissolution is actually zeroth order). Alternatively, letting the final condition be

$$r = 0 \text{ @ } t = t_d,$$

where t_d is the time it took to dissolve the crystal with starting radius of r_o , gives

$$r_o = kt_d,$$

which relates the total time to dissolution for a grain of initial radius r_o . Thus, the slope of the line passing through the data on a plot of r_o vs. t is the zeroth-order rate coefficient for the reaction (in other words, the slope of the line on the graph = k). If we measured grain size in mm and time in seconds, the slopes on our graphs have units of mm/sec. (Notice that, for tracking the size of an individual grain dissolving with time, the slope would be negative - the grain gets smaller with time. However, on our plot, we have plotted initial grain size *versus* time to complete dissolution. The slope on this plot is positive, which gives us a positive value of k , which is fine.)

You now have retrieved a zeroth-order/linear rate coefficient, and the regression coefficient, for the halite dissolution reaction from the lab data.

2. As Berner (1980) notes, one way to test whether the reaction is transport controlled is to calculate a theoretical rate for a transport process, and compare it to the actual rate. We now examine a simple equation for the spherically symmetrical diffusion-controlled dissolution of a single crystal.

The equation for diffusion-controlled growth of a small crystal completely surrounded by fluid (spherically symmetric case) is (Berner, 1980, Eq. 5-22):

$$\frac{dr}{dt} = \frac{D\nu(C_{inf} - C_{eq})}{r}$$

where r = crystal radius, t = time, D = the diffusion coefficient, ν = the molar volume of halite, C_{inf} = the concentration of Na (or Cl) in the solution at infinite distance from the crystal surface, and C_{eq} is the concentration of Na (or Cl) at equilibrium.

Integrate the equation between the limits

$$r = r_o \text{ @ } t = 0$$

and

$$r = 0 \text{ @ } t = t_d.$$

Solve for t_d as a function of r_o , rearrange for r_o as a function of t_d . Be sure to keep your dimensions consistent. How does the particle size scale as a function of time (linearly with time, as the square root of time, exponentially with time, etc.)? Diffusion-limited reactions

should exhibit a square-root of time dependence. Does your solution to the diffusion equation show this? Does the equation, and your solution, preserve appropriate signs? Why?

3. On a separate graph, plot your data for r_o vs. $t^{1/2}$ for your room-temperature trials.
4. On which plot do the experimental data more closely fit a straight line, r_o vs. t (problem 1) or r_o vs. $t^{1/2}$ (problem 3)?
5. Using your measurements of r_o for each individual run, assuming that the ambient concentration of Na^+ (or Cl^-) in the solution is zero, and rearranging your solutions to the diffusion equation as necessary, CALCULATE (theoretical) t_d for each run from your data. This is how long a grain of size r_o would take to dissolve in pure water, if the dissolution were controlled by spherically symmetrical diffusion (that is, if halite dissolution is transport controlled). Plot r_o vs. t as calculated, and plot your actual data (the same data you plotted in problem 1) on the same graph.

When applying the "best fit" line to your theoretical data, make sure you use the same model as you predicted in the previous question; that is, if you think the theoretical equation shows an exponential relationship between grain size and time of dissolution, apply that same concept to your data "fit." The model you choose should be obvious, that is, the mathematical equation tells you which model you must choose. Use the value of the tracer diffusion coefficient for sodium ion, D_{Na} , at infinite dilution (in water; Li and Gregory, 1974; Lerman, 1979);

$$D_{\text{Na}} = 1.33 \times 10^{-5} \text{cm}^2 \text{sec}^{-1}.$$

HINTS:

- What do you suppose would be the dimensions - units - of molar volume? Volume/mole, perhaps? There are at least three ways of getting this number, but everything you need to know about halite to do this is in most mineralogy textbooks.
 - You must also know the equilibrium concentration of Na^+ or Cl^- , which you can get from the solubility of NaCl . There are a number of ways of getting this (for example, you covered solubility equilibria in your intro chemistry class!), including looking it up (a number you can use more or less directly is actually in one of the assigned readings for this part of the course; there are others, too.). Whatever way you get it, justify the value you actually use, cite the sources of any numbers you use, and show all necessary work.
6. Repeat the previous step, using the value of the tracer diffusion coefficient for chloride, D_{Cl} , at infinite dilution (in water; Li and Gregory, 1974; Lerman, 1979);

$$D_{\text{Cl}} = 2.03 \times 10^{-5} \text{cm}^2 \text{sec}^{-1}.$$

7. Write approximately one page comparing the actual measured value of t_d from your experiments with the values calculated theoretically from the diffusion equation. Also, summarize your observations regarding the morphology of the halite crystals as they dissolve.

KINETICS PROBLEM SET: RATE LAWS FROM EXPERIMENTAL DATA II

1. Using a simplified dimensional analysis analogous to the Einstein-Bose equation,

$$L^2 = Dt$$

the characteristic length scale, L , for diffusion of Na and/or Cl ions away from the grain over the relevant time-scale (in this case, the duration of the experiment, t_d) can be calculated. Determine a characteristic length scale for diffusion of ions in the present experiment.

2. Diffusion is the slowest form of transport. However, advection (flow) is another, faster form of transport. Thus, a reaction could be transport controlled, but be faster than the diffusion-controlled rate, if flow rates are sufficiently high. Could advection be rate-determining in our experiments? Explain.

Estimate the velocity of water flow (cm/sec) past the dissolving halite grain in our experiment. Estimate how long it took for the water to penetrate as far as it did beneath the cover slip (seconds? tens of seconds?). Cover slip dimensions are 24 x 40 mm for the larger rectangular ones, or 22 x 22 mm for the small square ones.

The Peclet number, N_{Pe} (Domenico, 1977; see also Lerman, 1979; Berner, 1980, p. 117; Richardson and McSween, 1989) is

$$N_{Pe} = LU/D_i$$

where D_i is the diffusion coefficient, L is a characteristic length scale for the system of interest, and U is the flow velocity. The Peclet number is a dimensionless number (or dimensionless group) that permits us to evaluate whether advection/flow or diffusion is the dominant transport process in any specific case. If it is very small ($LU/D_i \ll 1$; $D_i \gg LU$), then diffusion is the dominant transport process; if it is very large ($LU/D_i \gg 1$; $LU \gg D_i$), then flow is the dominant transport process.

What is the Peclet number for our experimental system? Which transport process dominates in our experiments, advection (flow) or diffusion? Is movement of water - flow - the rate-determining factor in our experiment (in other words, what variable can you change that can give you larger or smaller Peclet numbers)?

3. Perhaps we need to be less restrictive in our assumptions than we were in using the equation for spherically symmetrical diffusion controlled growth and dissolution (problem 2 in the previous homework set); maybe the data show a non-linear time dependence different from the one predicted in that case.

Hodder (1990) reminds us that any equation for diffusion-limited, square-root-of-time kinetics can also be logarithmically transformed, allowing us to test whether the exponent is really $1/2$. For our case, a simplified form of the solution for the spherically symmetric diffusion controlled dissolution equation from the previous homework set is,

$$r(t) = r_0 - kt^{1/2} \quad \text{giving} \quad r_0 = kt^{1/2}$$

for time to complete dissolution of a grain of initial radius r_0 . The base 10 logarithmic transformation of this equation is

$$\log_{10} r_0 = 0.5 \log_{10} t + \log_{10} k.$$

Once again, this is the equation for a straight line ($y = mx + b$) on a plot of $\log_{10} t$ on the x -axis and $\log_{10} r_0$ on the vertical axis. Create this log-log plot of your data, and determine the slope of the best-fit line. If the slope is 1.0 (within experimental error), the data obey a linear relationship between of size and time (that predicted from a zeroth-order rate law). If the slope is 0.5 (within experimental error), the data obey a parabolic (square root of time) dependence of size with time (like that predicted from diffusion equations). If the slope is not 0.5, the dependence of rate on time is not the parabolic one predicted by diffusion equations, and perhaps some process other than diffusion is rate-determining.

4. Do the experimental data plot as a straight line on any of the plots you've made so far? You can probably force a straight line through each of the data plots. Is any one of them a "better" fit to the data? (The scatter of the data is probably too great to tell.) Recall that a square-root-of-time relationship has often been interpreted as a basis for concluding that the reaction is diffusion-limited. Can you draw any preliminary inferences from the various data plots & theoretical & regression lines/curves?
5. Nielsen (1964; see reference in Berner, 1980) derives a relationship for surface-controlled precipitation, where a layer of material grows as soon as a single surface nucleus forms (mononuclear layer mechanism). If we assume a similar mechanism can operate during dissolution (that is, that an entire layer of the dissolving mineral dissolves as soon as the first successful dissolution site forms, and before the next successful dissolution site forms), changing the sign in Nielsen's equation gives

$$dr/dt = -kr^2$$

Because surface area scales with r^2 , this is roughly equivalent to saying that the dissolution rate is proportional to surface area; the number of active sites for nucleation of dissolution centers (etch pits) is proportional to surface area - which is a good first approximation for an interface-controlled reaction.

Integrate the equation between the limits

$$r = r_0 \text{ @ } t = 0 \quad \text{and} \quad r = r \text{ @ } t = t.$$

Solve for t as a function of r , rearrange for r as a function of t . According to this equation, what happens to the dissolution rate as the radius of the crystal becomes small? Is this a physically reasonable result? If necessary, ignore the range over which r is small. Make an appropriate plot of the data, and retrieve the "mononuclear interface-limited" rate coefficient. The data appear to be too "messy" to determine a single best-fit relationship; however, if you were working for an environmental consulting firm or petroleum exploration firm, you wouldn't have time to wait for more research to give you the "right" answer. Quite often in cases such as this, if selecting among different equations is difficult to justify, it is sometimes the custom to just choose the simplest rate law. Up to and including this homework, you have now examined several cases; (i) a (highly oversimplified) zeroth-order rate law; (ii) a simple (empirical) parabolic rate law; (iii) a theoretically derived rate law explicitly involving diffusion as the rate-determining process; and (iv) a rate law for one possible simple interface-limited case. Which relationship, if any, best describes the data set? Choose your rate equation carefully. Choosing the most useful rate law, even if based on limited data, is required for remediation or exploration. On the basis of your attempts at modeling, what process(es) is(are) rate-determining in the dissolution of halite? What other observations have you made that are relevant to the question of the rate-determining step in halite dissolution? What conclusion do those observations support? Emphasize possible sources of error in the experimental design, and in applying the various equations to the actual experiment.

IMPORTANT NOTES ON THE KINETICS PROBLEM SETS

These homework exercises use the measurements you made in the room-temperature halite-dissolution lab to explore the rate law and the rate-determining mechanism for the dissolution of halite in pure water.

- We actually measured the length of one side of a cube. For many of the equations, it would be simpler to deal with a sphere; a sphere with the same diameter as the length of our cube (d) would have a radius $r = d/2$.

- To do many of the following problems, you must determine the slope of the best-fit straight line that passes closest to all the points. Remember, the equation for a straight line is $y = mx + b$. There are several ways you might do this: (i) use any computer program you might have access to (e.g., Excel, Lotus 1-2-3, Cricket Graph, etc.) to calculate the linear least squares regression line; or (ii) do the same thing on your calculator (yours may even have this as a function; if not, there are formulas in some math books).

- In some problems, you are not given all the information required to solve the problem. However, if you think about the dimensions (units) of the number you are trying to calculate, and of the numbers you are given in the problem, you can determine the units of the missing information. Usually (in all cases in these homework sets), once you know what you are looking for, it is pretty easy to put together information you have access to (e.g., in your textbooks or other assigned class readings) to get the information you need to complete the problem.

- You are almost all science majors, so you shouldn't have to be warned about this, but be *extremely* careful when converting units. Also, beware of dimensions in any numbers you need to look up. You may find the number you are looking for, but its dimensions may not be exactly the units you're looking for. Incorrect conversions of mm to cm, diameter to radius, liters to cm^3 , grams to moles, and so on, are the biggest mistakes students make in these homework exercises.

- If you look up a number, and it's wrong, *you* are responsible. (Similarly, if you look up the right numbers, but your calculations are wrong, *you* are responsible.) Your consulting firm is liable for erroneous recommendations made to a client, regardless of why the error was made, so your calculations **MUST** be correct. Bad recommendations are bad business for your company. That's why you **MUST** double check any numbers used in your calculations, **AND** the calculations themselves.

The limits of integration for all parts of this exercise are (unless otherwise stated)

$$r = r_0 \text{ @ } t = 0 \quad \text{and} \quad r = r \text{ @ } t = t,$$

where r_0 is the radius of the crystal at the start of the experiment ($t = 0$), and r is the radius at any specified t time after the start of the experiment. In some cases, we will specify the final condition

$$r = 0 \text{ @ } t = t_d,$$

where t_d is the time it took to dissolve a crystal of starting radius r_0 .

Berner (1978, 1980, 1981) states that dissolution reactions are either transport-controlled (that is, some transport process governs the rate of dissolution) or interface-controlled (a reaction process at the mineral-solution interface is rate-determining). There are at least 4 possible "tests" for identifying the rate-determining mechanism (in no particular order of importance): (1) Stirring (advection/flow-rate/flushing-rate) dependence (for transport-controlled) or lack thereof (for interface-controlled) of the reaction rate (Berner, 1978); (2) Comparison and "goodness of fit" of theoretical equations to the experimental data; (3) Grain morphology; (4) The Arrhenius activation energy of the process (Berner, 1978; Lasaga, various). We will investigate the first three here.

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NOTES TO THE INSTRUCTOR

OBJECTIVES

This module consists of a laboratory exercise and related homework problems on geochemical kinetics of mineral-solution reactions for undergraduate mineralogy. Students measure the grain sizes of equant halite crystals, and the time for complete dissolution of each grain. From these data, students retrieve a rate law, from several possible. Additional homework problems allow various chemical and physical transport processes in mineral-fluid systems to be evaluated.

The lab and homework illustrate several basic principles of chemical kinetics directly relevant to geology, including rate laws of reactions, diffusion, advective transport, and the relationship between rate-limiting mechanisms and crystal-surface morphology.

REQUIRED BACKGROUND

A treatment of chemical kinetics (rate laws, diffusion) equivalent to that of chapter 3 in Gill (1995) is assumed. I also require the students to read Berner (1978), for its emphasis on low-temperature aqueous reactions. Treatments comparable to either or both of these references are found in Brownlow (1996, p. 210-213 and p. 355-365), Krauskopf and Bird (1995, ch. 11), Drever (1988, ch. 7; 1997, ch. 11), Langmuir (1997, ch. 2), Faure (1991, ch. 19), and Henderson (1982, ch. 8). The treatments in Berner (1980, p. 78-79; 1981, ch. 3), Sposito (1994, secs. 1.3-1.5, 3.1 & 4.5), Lasaga (1981, ch. 1), Richardson and McSween (1989, chs. 5 & 10), Stumm (1992, chs. 5 & 6), Stumm and Morgan (1996, ch. 2 p. 58-87 & ch. 13), Nahon (1991, ch. 1) and Lerman (1979, chs. 3 & 5) are more advanced. Cussler (1984) is a superb treatment of diffusion.

The treatment of kinetics in Gill (1995), Krauskopf and Bird (1995), Henderson (1982), and Richardson and McSween (1989) emphasize applications to igneous and metamorphic rocks; the other references emphasize weathering, diagenesis, and aqueous geochemical applications. These textbooks and journal articles, and other resources useful for or cited in the homework exercises, are included in the reference list.

EQUIPMENT & LAB MANAGEMENT

The exercise requires microscope stations each consisting of equipment readily available in most science departments: a petrographic microscope with a graduated reticle; beakers, medicine droppers, glass slides, cover slips, water (preferably distilled); a thermometer; a timepiece good to the nearest second (a wristwatch will suffice); and table salt. Students work in pairs in the laboratory, alternating tasks. One member manipulates the experimental materials, the other times the runs and records the data. Students can generate a dozen or more trials during one two-hour lab period. There must be half as many stations as students in the largest lab section.

The most critical material factor noted to date in the success of the exercise is the morphology of the initial halite crystals. Much individually packaged salt from "fast-food" restaurants has skeletal morphology, which makes measurement of a useful grain size impossible. Bulk grocery store table salt is generally perfect cubes. Data scatter decreased noticeably when equant crystals

were introduced. Select only grains with cross-sections as close to a perfect square as possible. Do *not* use irregularly shaped single grains, or clumps of grains.

As wide a range of grain sizes should be used as the sample permits.

Stabilize the temperatures of the beakers of water and other items before the lab; allow as much as one full day. Temperature drift during the lab period can be an important source of error.

HOMEWORK MANAGEMENT

I usually give a preparatory homework assignment, to familiarize students with some of the quantitative aspects of kinetics prior to actual data reduction, and to allow them to make their "dumb" mistakes (unit conversion errors, &c.) early. Most of these problems come directly, or are adapted, from the geochemistry textbooks listed above. I also ask the students to perform a few simple indefinite and definite integrations (to review their elementary calculus skills). Homework problems involving first-order kinetics can be adapted from any treatment of radioactive decay. Basing the "rate law" review and the "calculus review" on the students' presumed familiarity with radioactive decay works well; if they understand any rate law at all from their previous geologic background, it's exponential decay.

The subsequent homework exercises included here use the student-generated data to retrieve a simple rate law for the dissolution of halite in pure water, and to investigate the possible influence of several transport processes.

For truly mathophobic students, the instructor can supply any or all integrated forms of rate laws.

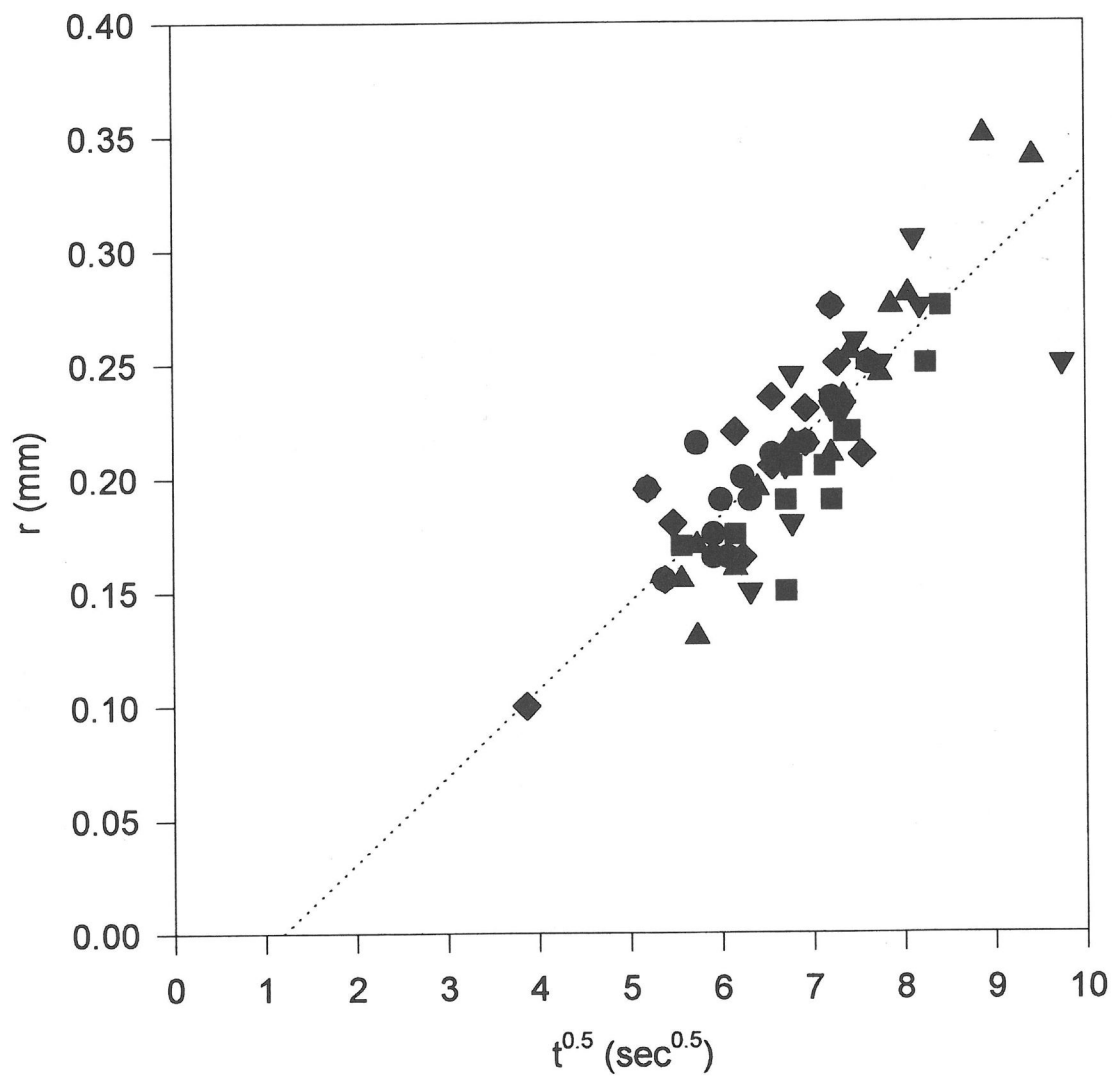
Diffusion is well treated in most available geochemistry textbooks. Advective transport properties are usually not covered until the fluid-flow part of sedimentology, or possibly in really process-oriented petrology texts and courses, but all that one needs to know for the present purpose is the dimensions of velocity. The last homework set is pushing the envelope for a one semester class; I last used it only for extra credit.

The instructor can supply the solubility of halite. Alternatively, if the students have already had some equilibrium thermodynamics, they can calculate the solubility from Gibbs free energies. Finally, the instructor can turn this into a resource-search exercise, and have the students find the solubility of halite in some reference.

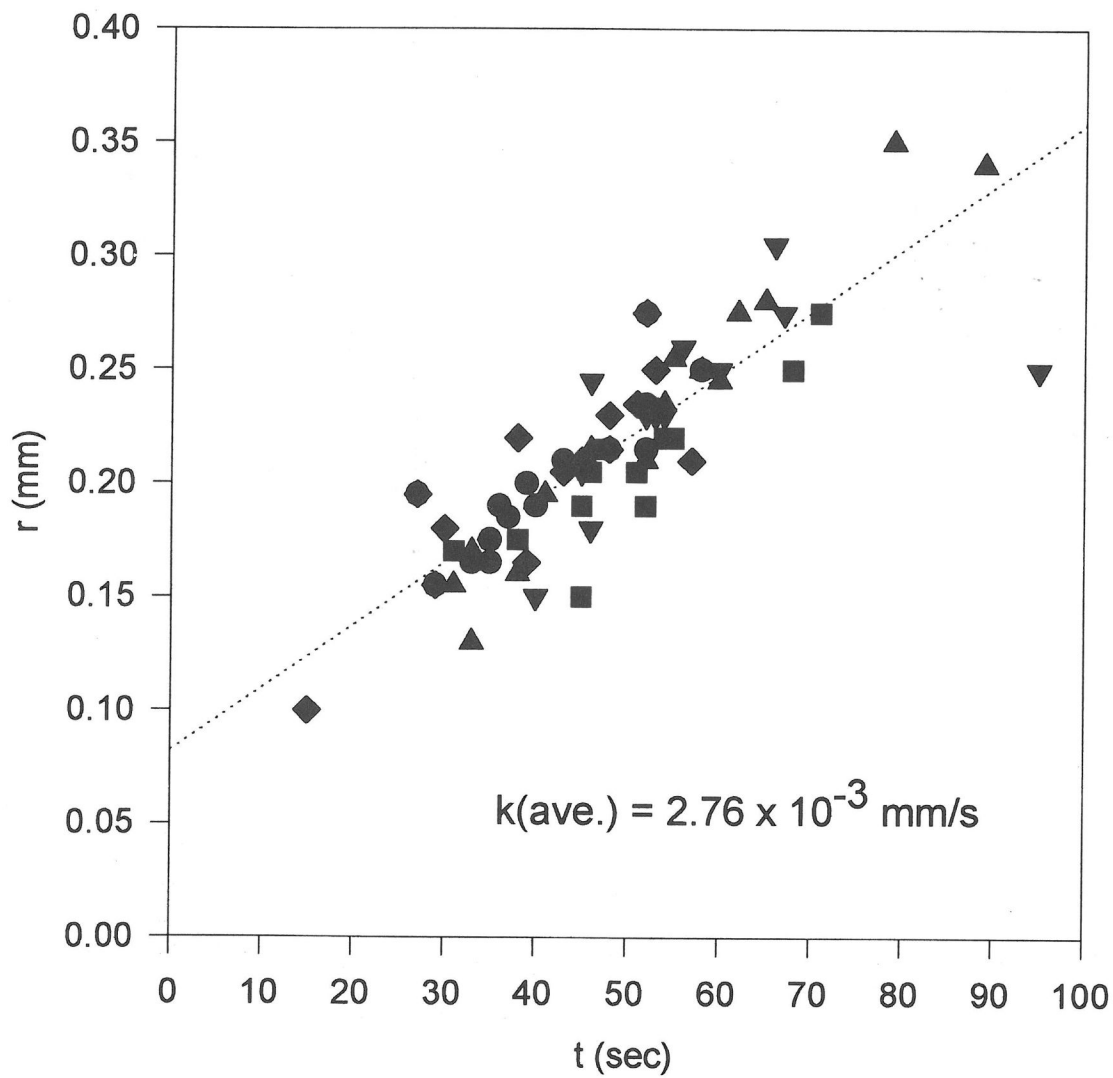
ACKNOWLEDGEMENTS

The assembly of this exercise was facilitated by my participation in the NSF Workshop on Teaching Mineralogy (NSF DUE UFEP 95-54635, to J.B. Brady). Numerous students and graduate teaching assistants helped me refine these exercises over the years, and I am grateful to all of them. I would especially like to thank John B. Sallman III for his extensive editorial contributions to making the student instruction sets more "user friendly," and to Troy Holcomb, Tracy Pierce, Neil Steinkamp, Ryan Thies, Brad Batchelor, and James Cross, for their independent efforts to extend the scope of these experiments.

**Halite dissolution, 20-22°C (5 datasets)
Square-root-of-time (parabolic) plot**



**Halite dissolution, 20-22°C (5 datasets)
Linear plot**



HEAT CAPACITY OF MINERALS: A HANDS-ON INTRODUCTION TO CHEMICAL THERMODYNAMICS

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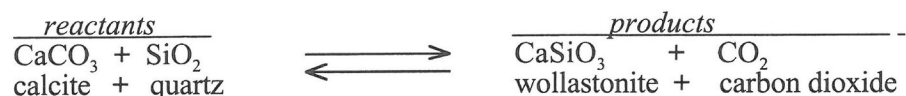
INTRODUCTION

Minerals are inorganic chemical compounds with a wide range of physical and chemical properties. Geologists frequently measure and observe properties such as hardness, specific gravity, color, etc. Unfortunately, students usually view these properties simply as tools for identifying unknown mineral specimens. One of the objectives of this exercise is to make students aware of the fact that minerals have many additional properties that can be measured, and that all of the physical and chemical properties of minerals have important applications beyond that of simple mineral identification.

ROCKS AS CHEMICAL SYSTEMS

In order to understand fully many geological processes, the rocks and the minerals of which they are composed must be viewed as complex chemical systems. As with any natural system, minerals and rocks tend toward the lowest possible energy configuration. In order to assess whether or not certain minerals are stable, or if the various minerals in the rock are in equilibrium, one needs to know how much energy exists in the system, and how it is partitioned amongst the various phases.

The energy in a system that is available for driving chemical reactions is referred to as the **Gibbs Free Energy (GFE)**. For any chemical reaction, the reactants and the products are in equilibrium (i.e., they all are stable and exist in the system) if the GFE of the reactants is equal to that of the products. For example:



$$\begin{aligned} \text{at equilibrium: } (G_{\text{calcite}} + G_{\text{qtz}}) &= (G_{\text{wooll}} + G_{\text{CO}_2}) \\ \text{or: } \Delta G &= (G_{\text{reactants}} - G_{\text{products}}) = 0 \end{aligned}$$

If the free energy of the reactants and products are not equal, the reaction will proceed to the assemblage with the lowest total energy.

Being able to assess chemical equilibrium and phase stability is extremely important in many fields of geoscience. In order to do this, a number of fundamental properties of the chemical system, and of the phases in the system, must be known. Obviously, the temperature (T) and pressure (P) of the system are two of the most important variables. In order to evaluate the GFE of a system, two additional variables must also be known -- the **enthalpy (H)** or thermal energy content of the system, and the **entropy (S)** or degree of disorder of the system. The relationship between the free energy, enthalpy, and entropy of a chemical reaction is given by:

$$\Delta G = \Delta H - T\Delta S$$

Today we will examine the **enthalpy** of chemical systems.

HEAT AND THERMAL ENERGY

Energy exists in many forms - electrical, thermal, and mechanical. Energy can be transformed from one form to another but it cannot be created or destroyed; energy is always conserved. Heat is thermal energy that passes from a substance at high temperature to a substance at a lower temperature.

The enthalpy, or total thermal energy content, of a system (or phase) is largely a function of temperature; the higher the temperature of a substance, the more thermal energy it possesses. In addition, the thermal energy of a substance is also a function of the amount of substance. In other words, enthalpy is an **extensive** variable -- it depends upon the amount (or extent) of matter involved.

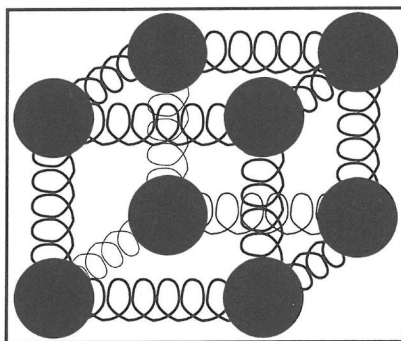
Enthalpy, however, is not simply a function of temperature and mass. For example, if you were to take 100 g of water and 100 g of quartz and heat both to 50° C, they would not contain the same amount of thermal energy. This is because different materials have different capacities for storing thermal energy. This capacity for storing thermal energy is referred to as the **heat capacity** (C_p) of the substance. The relationship between enthalpy (H), temperature (T), and heat capacity (C_p) is given by:

$$\Delta H = C_p * \Delta T$$

or, in words: the total thermal energy content of a substance changes directly as a function of changes in the temperature of the system, times the heat capacity of the material (at constant pressure).

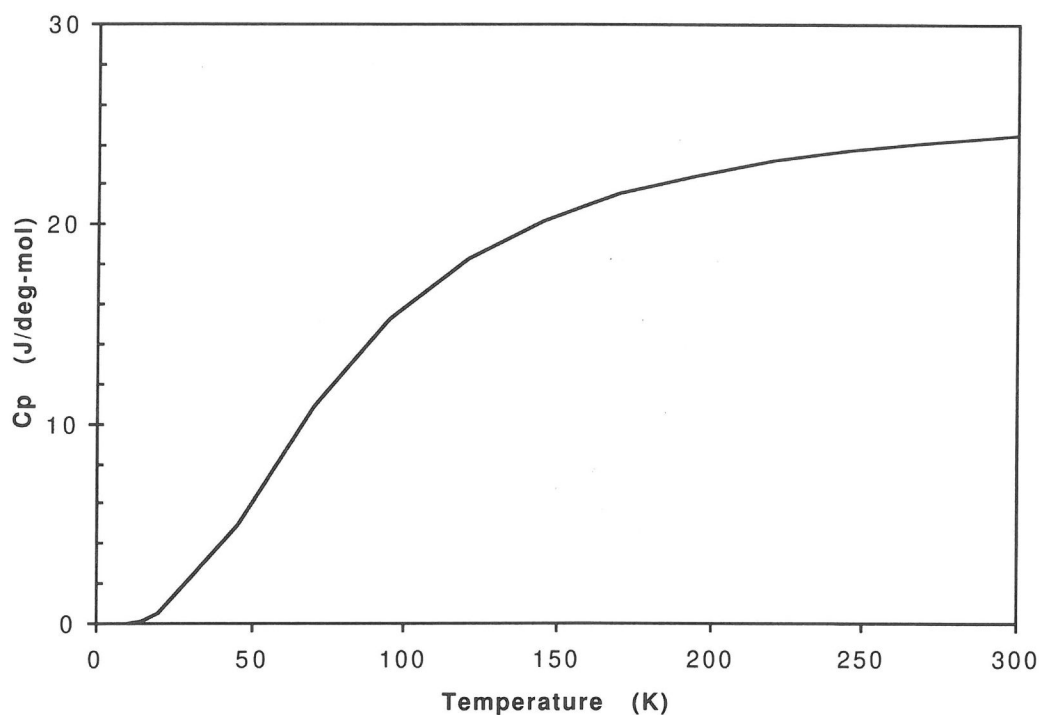
Heat Capacities of Minerals

Minerals are crystalline solids. On an atomic level, each atom in a crystal structure resides in an equilibrium position known as a *lattice site*. At any temperature above absolute zero, atoms have kinetic energy; that is, they don't just sit in a lattice site, they move about, "bouncing" off of adjacent atoms. To a first approximation, individual atoms in a crystal lattice can be considered to be 3-D harmonic oscillators. Imagine that the atoms of a solid vibrate, much as if they were bonded to one another with springs -- as is illustrated in the sketch of a simple cubic lattice cell below.



At absolute zero, the atoms of a perfect solid can not vibrate, thus the heat capacity of the substance, and the total enthalpy are zero. The atoms of a solid can vibrate collectively to progressively greater extents as the temperature is increased; thus, the heat capacity of a substance increases with increasing temperature. For most substances, there is an upper limit to this capacity (see graph on following page), and this limit is commonly attained at temperatures well-below room temperature.

Heat Capacity of Copper vs. Temperature



In the experiment described below, you will measure the heat capacity of a variety of elemental metals and simple polyatomic mineral compounds. You will then be asked to evaluate the precision and accuracy of your data, and to identify some of the factors that influence the heat capacities of crystalline solids.

Units.

The units to be used in the following experiment are:

Mass:	gram (g)
Temperature:	Celsius ($^{\circ}\text{C}$) or kelvin (K); where $^{\circ}\text{C} = \text{K} - 273.15$
Thermal energy:	joule (J); (1 cal = 4.186 J)
Amount of substance:	mole (mol)
Volume:	cubic centimeter (cm^3)
Density:	g / cm^3
Molecular weight:	g / mole

HEAT CAPACITY OF CRYSTALLINE SOLIDS

Part I. Measuring Heat Capacity

By definition, the *heat capacity* * of a substance is the amount of heat needed to raise the temperature of one gram of the material by 1 °C. Thus, the units for heat capacity are:

$$C_p = \text{J} / ^\circ\text{C}\cdot\text{g}$$

Similarly, the *molar heat capacity* of a substance is the ratio of the heat supplied to a mole of substance to its consequent rise in temperature.

$$C_p = \text{J} / ^\circ\text{C}\cdot\text{mol}$$

Relative heat capacities (specific heats*) can be determined by placing two materials, each initially at a different temperature, in contact with each other. Because energy is always conserved, and because heat flows from warmer materials to colder materials, heat will flow between the two materials until the two are in thermal equilibrium. At this point, the thermal energy lost by the initially warmer object must equal the thermal energy gained by the cooler object:

$$(\text{joules lost})_{\text{hot object}} = (\text{joules gained})_{\text{cold object}}$$

Because the change in thermal energy content of each substance is equal to the heat capacity of each object times the change in temperature and the mass of each substance, we get:

$$(C_p \times \text{mass} \times \Delta T)_{\text{hot object}} = (C_p \times \text{mass} \times \Delta T)_{\text{cold object}}$$

In the experiment that you will perform, you will heat various solids (of known mass) in a hot water bath (of known temperature) until the materials come into thermal equilibrium with the hot water. You will then transfer each sample individually into a beaker containing a known mass of water at a known, lower temperature. The highest temperature reached after you have transferred the material into the water is then taken as the temperature at which thermal equilibrium was achieved. Because the heat capacity of water is known, the only unknown in the equation above is the heat capacity of your sample. Rearranging the equation:

$$\frac{C_{p \text{ sample}}}{C_{p \text{ water}}} = \frac{(\text{mass} \times \Delta T)_{\text{water}}}{(\text{mass} \times \Delta T)_{\text{sample}}} = \text{S.H.}_{\text{sample}}$$

Note that the units in the above equation cancel out. The number you end up with is referred to as the “*specific heat*” of the substance (analogous to the *specific gravity* measurements we make with the Jolly balance). You can convert your specific heats into heat capacities by multiplying by the heat capacity of water:

$$C_{p \text{ sample}} = \text{S.H.}_{\text{sample}} \times C_{p \text{ water}} \quad \text{where: } C_{p \text{ water}} = 4.186 \text{ J} / \text{deg}\cdot\text{g}$$

[* - The terminology can be confusing. While “thermal capacity”, “heat capacity”, and “specific heat” are often used interchangeably, for this exercise I will follow the CRC handbook definitions and use “thermal capacity” and “heat capacity” as synonyms (units of J/deg-g); “specific heat” will be used only to refer to the relative heat capacities of substances (unitless).]

Procedure.

1. Work in groups of three in lab. Everyone must record the data and turn in a completed lab exercise and write-up.
2. Make sure you have the necessary supplies:
crystalline solids (provided by instructor)
two Styrofoam cups
a large beaker of boiling water
two thermometers (one 0 to 110 °C thermometer, and one 0 to 50 °C thermometer)
3. Weigh your mineral / metal samples. Record the weights in the tables provided.
4. Suspend the materials in the beaker of boiling water. Record the temperature of the boiling water.
5. Nest together two dry and clean Styrofoam cups. Record the weight of the empty cups. Fill with approximately 50 ml of room temperature water and re-weigh.
6. When your solid sample has reached thermal equilibrium with the boiling water, quickly transfer the sample from the hot water bath to the room temperature water in the Styrofoam cups.
7. Stir and note the maximum temperature reached by the system (water + sample).

PART II. Heat Capacities of Elemental Metals

First the class will measure the heat capacities of six different elemental metals: Al, Si, Fe, Cu, Ag, and Pb. Each group will measure the heat capacities of all six metals. Follow the procedure above and record your data below.

	Metal				Water			
	weight (g)	T initial (°C)	T final (°C)	ΔT (°C)	weight (g)	T initial (°C)	T final (°C)	ΔT (°C)
Al								
Si								
Fe								
Cu								
Ag								
Pb								

PART II. Heat Capacities of Elemental Metals (cont.)

Calculate the gram and molar heat capacities of your samples using your data, and the data collected by your classmates. Calculate and record the mean heat capacity values, along with the standard deviation of each value.

	Al	Si	Fe	Cu	Ag	Pb
Cp (J/deg-g)						
Cp (J/deg-mol)						
Density (g/cm ³)						
Mol. Weight (g/mol)						

Questions

1. Is the heat capacity of elemental metals primarily a function of the mass of the individual atoms? Construct a graph of the molar heat capacities vs. the molecular weights of the six metals. Is there a positive correlation between molecular weights and molar heat capacities?
2. Is the heat capacity of elemental metals primarily a function of the density of the metal? Construct a graph of the molar heat capacities vs. the densities of the six metals. Is there a positive correlation between densities and molar heat capacities?
3. Is the heat capacity of elemental metals primarily a function of the number of atoms (moles) per unit volume? Construct a graph of the number of atoms per cubic centimeter (moles/cm³) vs. the volume heat capacity (J/deg-cm³) of the elemental metals. Is there a positive correlation between # of atoms and heat capacities? (Note: Calculate the volume heat capacities by multiplying the specific heat capacities of each metal by their densities; you should end up with units of J/deg-cm³).
4. Using the volume heat capacities calculated above, note which of the six metals would be best for storing the most amount of thermal energy per unit volume?
5. Most of the metals have molar heat capacities on the order of 25 J / deg-mol, regardless of density and/or molecular weights! Thus, for most metals (and in fact, for most crystalline solids), the heat capacity of the substance is primarily a function of the total number (moles) of atoms present. The accepted heat capacities of the six metals are (in J / deg-mol): Al - 24.4; Si - 20.0; Fe - 25.1; Cu - 24.4; Ag - 25.4; Pb - 26.4). How do these values compare to the values measured in class? If they differ, discuss possible reasons for the observed discrepancies. What are some of the sources of error in our measurements?
6. Diamond (C) has a molar heat capacity of 6.12 (J / deg-mol). Our results for the metals above suggested that the heat capacity of a substance was primarily a function of the number of atoms (approx. 25 J / deg-mol). Why then does diamond have such a significantly different molar heat capacity? What might explain the unusually low heat capacity of diamond? (Hint: In what way does diamond differ from the metals discussed above?)

PART III. Heat Capacities of Minerals

Most minerals are polyatomic crystalline solids. In detail, the heat capacities of polyatomic solids are a function of many complex factors (e.g. quantum state, mass, nature of bonding, etc.). Fortunately, to a first approximation, the heat capacities of polyatomic solids are essentially just the sums of the heat capacities of the constituent atoms. An empirical list of the atomic contributions to the heat capacities of polyatomic solids was first compiled by Kopp in 1865. A list of the “Kopp parameters” is given below (from Winn (1995) and Berry et al. (1980)):

<u>Atom</u>	<u>Cv (J / deg-mol)*</u>
H	10.5
Be	12.5
B	10.5
C	8.4
N	12.5
O	16.7
F	20.9
Al	14.5
Si	15.9
P	22.7
S	22.7
All heavier elements:	25.9

(*Note: These are values for the heat capacity at constant volume. All previous values were for constant pressure. Fortunately, for most crystalline solids, $C_v \sim C_p$. For the rest of this exercise, you may use the values above to estimate heat capacities of solids at constant pressure.)

Let’s run through an example of how the Kopp parameters can be used. For quartz, the heat capacity calculated using the Kopp parameters is:

$$\begin{array}{rclcl} \text{Cp silicon} & + & (2 \times \text{Cp oxygen}) & = & \text{Cp qtz} \\ 15.9 & + & 33.4 & = & 48.9 \text{ J / deg-mol} \end{array}$$

The accepted value for quartz is 44.5 J / deg-mol. This is a fairly typical result; usually within 10% of the accepted value.

PART III. Heat Capacities of Minerals (cont.)

First we will measure the heat capacities of six different minerals: three oxides and three sulfides. Each group will select one of the minerals, and will make five separate measurements of the heat capacity of their sample. Follow the procedure you used for the metals and record your data below.

Mineral: _____ Formula: _____

Molecular weight: _____ Density: _____

Trial	Mineral				Water			
	weight (g)	T initial (°C)	T final (°C)	ΔT (°C)	weight (g)	T initial (°C)	T final (°C)	ΔT (°C)
#1								
#2								
#3								
#4								
#5								

Calculate the specific heat (S.H.) and the gram and molar heat capacities of your sample using the data above. Record your results below.

Mineral: _____

Trial #:	S.H.	Cp (J / deg-g)	Cp (J / deg-mol)
1			
2			
3			
4			
5			
Mean			
s.d.			

PART III. Heat Capacities of Minerals (cont.)

Estimate the molar heat capacities of the six minerals using the Kopp parameters. Record these values in the table below. In addition, record the mean heat capacity values for each sample as determined by the class.

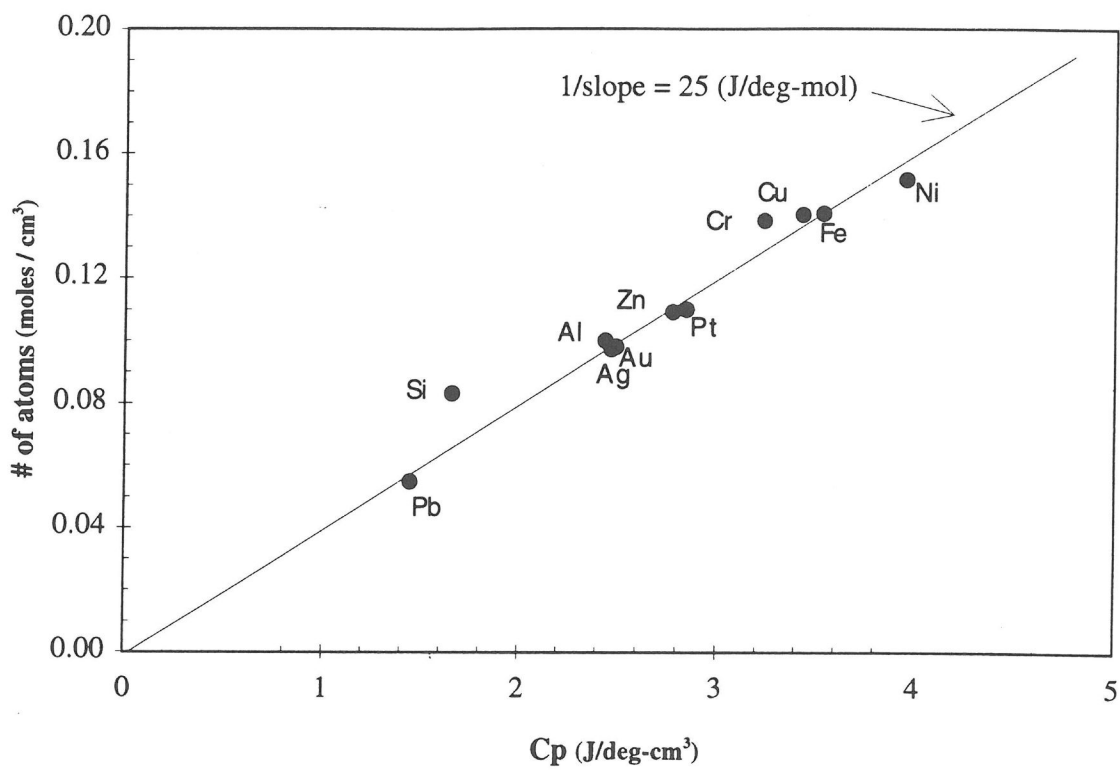
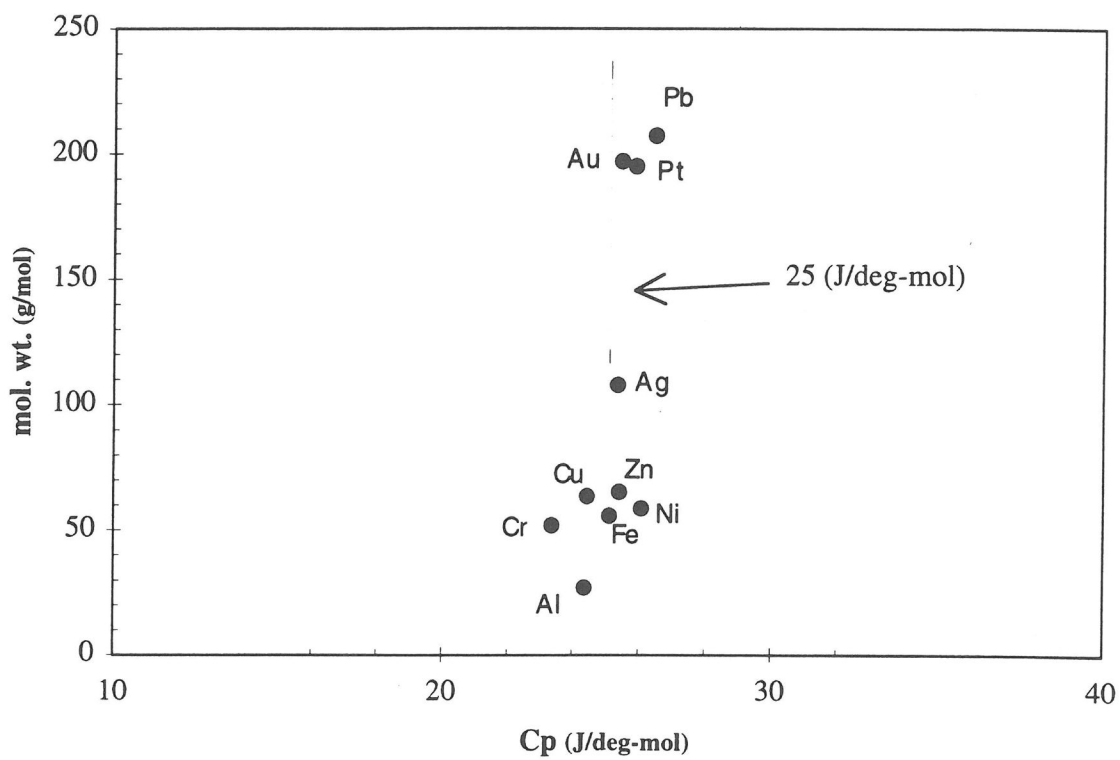
	Cp (J / deg-mol)		
	Accepted values	Kopp values	Measured values
galena	49.5		
sphalerite	46.1		
pyrite	62.2		
quartz	44.5		
corundum	79.1		
magnetite	143.5		

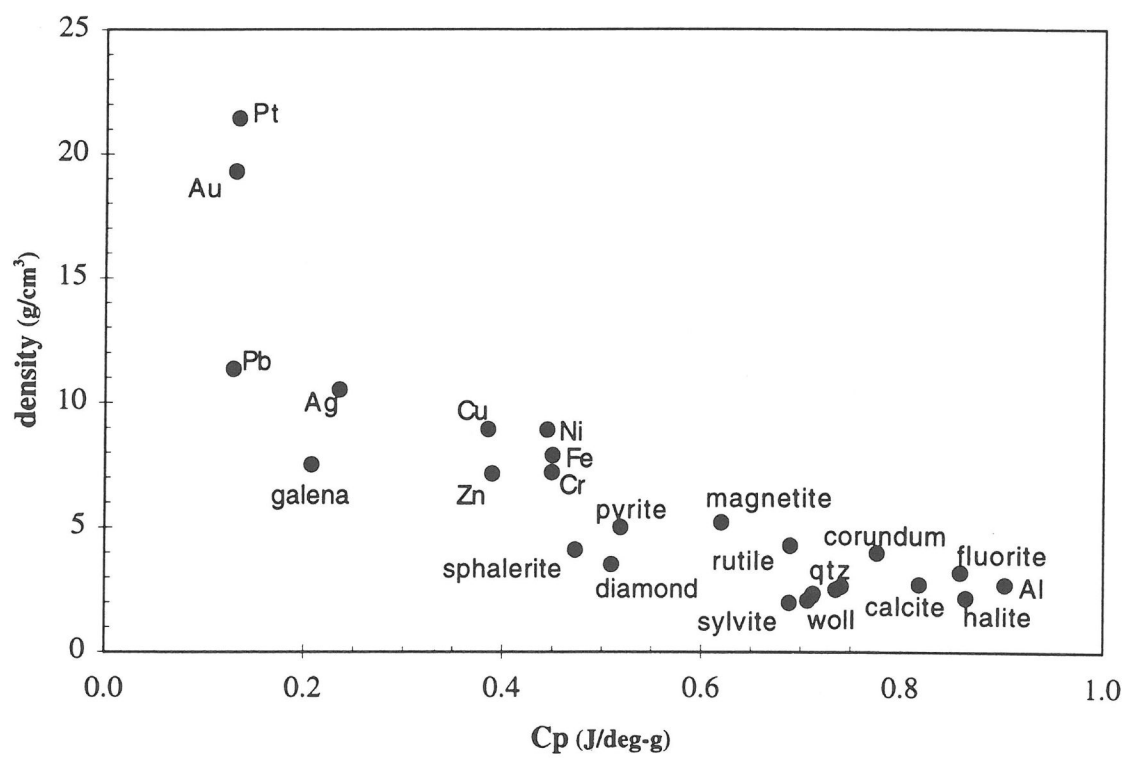
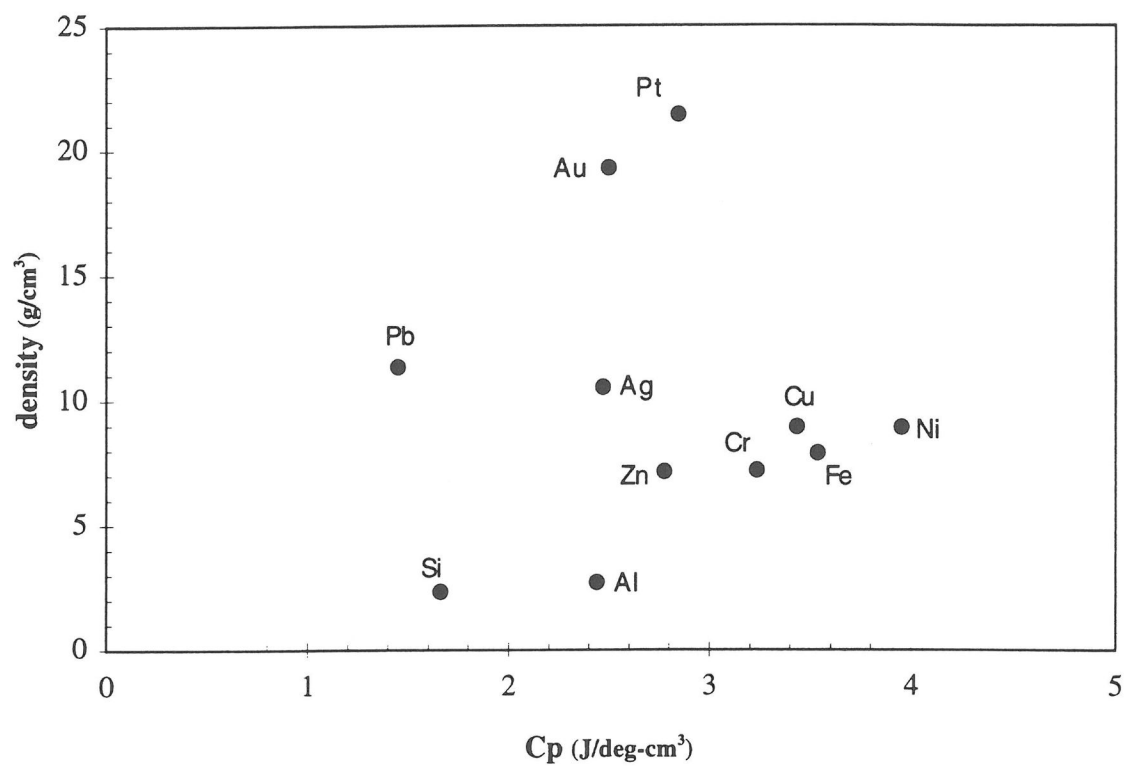
Questions

1. Compare the measured molar heat capacity values for these minerals with the predicted values (using the Kopp parameters) and the accepted values. Do the measured values correlate with the predicted / actual values? If not, discuss possible reasons for the discrepancies.
2. Attached is a plot of the volume heat capacity (J / deg-cm³) vs. the # of atoms per cm³ for a variety of elements. (Note that the slope of the “best fit” line corresponds to the average Kopp parameter for heavy elements ~ 25 J / deg-mol). On the basis of this plot, what solid material can store the most thermal energy per **cubic centimeter**?
3. Attached is a graph of heat capacity vs. the density of a variety of elements and minerals. On the basis of this plot, what solid material can store the most thermal energy per **gram**?
4. Considering that (in general) metals can store more thermal energy per cubic centimeter and/or per gram than most other solids, why aren't they commonly used as “heat sinks” in passive solar applications? Try to come up with at least three good reasons! (Hint: Think about how **time** might be an important factor!)
5. If you were to take a 1 m³ rock composed of quartz, and a second 1 m³ rock composed entirely of magnetite, how much thermal energy would you need to add to each to increase their temperature by 100 °C? Show your work.

REFERENCES

- Berry, R.S., Rice, S.A., and Ross, J., (1980), Physical Chemistry, John Wiley & Sons, New York, NY.
Winn, John S., 1995, Physical Chemistry, Harper Collins College Publishers, New York, NY.





PHASE DIAGRAMS IN VIVO

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INTRODUCTION

Fluid Inclusions

All solids crystallizing from a liquid phase trap small, accidental amounts of the parent liquid in features we call fluid inclusions (Fig. 1). Fluid inclusions typically range in size from less than 1 micron to several hundred microns and are easily seen in transparent minerals with a standard high-power petrographic microscope (200 to 400X, condenser in). Excellent fluid inclusions can be found in almost any sample of fluorite (cleave off a fragment no more than 2 mm thick) and quartz.

Fluid inclusions are time capsules that preserve small volumes of the liquid from which the mineral precipitated. By studying the contents of a fluid inclusion using simple heating / freezing experiments the temperature and pressure at which the mineral formed can be determined. The density and composition of the fluid can also be determined directly! In recent years it has become possible to extract the fluid from single inclusions and determine its isotopic composition and in some cases its age. Fluid inclusion studies, therefore, provide a wealth of data and are used to decipher the P-T-t-p history of mineral and rocks.

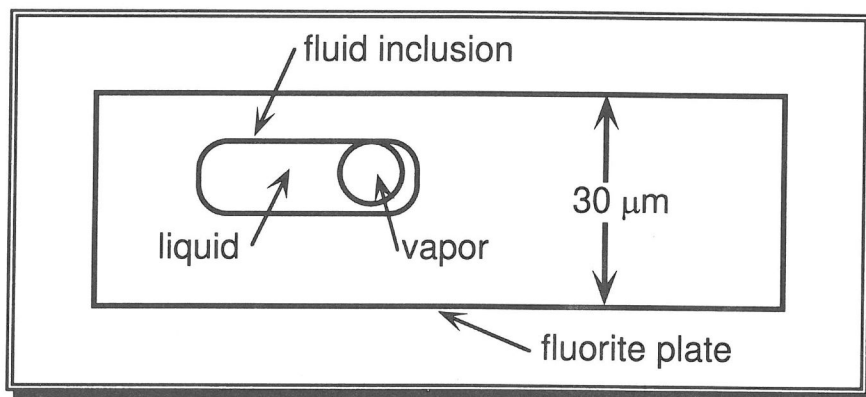


Figure 1. Idealized photomicrograph of fluid inclusions in fluorite at room temperature. Natural inclusions containing a low salinity fluid trapped above room temperature typically contain two phases-- aqueous fluid and vapor bubble. The bubble is actually a “shrinkage” phenomenon. Assume an aqueous fluid was trapped at 250°C. The fluid would have a density of 0.8 gm/cm³. As the temperature drops both the host fluorite and the aqueous fluid will contract (thermal expansion). It is well known that solids have the least thermal expansion and that gases have the greatest thermal expansion. Liquids are intermediate but closer to solids. As the temperature reaches room temperature the density of the liquid increases to 1.0 gm/cm³ (assume that nothing enters or leaves the fluid inclusion). Over the temperature range considered the density and volume change of the fluorite is negligible. Since the mass of fluid remains constant while the density increases it follows that the volume must decrease (volume = mass / density). The fluid separates into a vapor and fluid phase such that the total mass remains the same at room temperature ($\text{vol}_{\text{vapor}} * \text{density}_{\text{vapor}} + \text{vol}_{\text{fluid}} * \text{density}_{\text{fluid}}$) as at the entrapment temperature ($\text{vol}_{\text{fluid}} * \text{density}_{\text{fluid}}$). What must the volume of the bubble be if the density of the vapor is 0.01 gm/cm³?

The significance of fluid inclusions was recognized early on but quantitative results from fluid inclusion studies awaited the completion of laboratory experiments in geologically relevant systems. In an interesting turn of events many laboratory experiments are now carried out using synthetic fluid inclusion as the experimental vessels. The advantage of using synthetic fluid inclusions rather than steel pressure vessels is that the contents can be examined visually at all times, equilibrium is established faster (lower mass), safety is greater (lower volume), and cost is lower.

Phase Diagrams for Brines, Magmas, and Minerals

Phase diagrams summarize experimental and/or observational data on mineral associations and mineral (and fluid) compositions. These data are used to deduce mineral reactions and to quantify geochemical variables in mineral reactions (T, pH, P, bulk composition, X_{mineral} , X_{fluid} , etc.). There are many types of phase diagrams (pressure - temperature, temperature - pH, activity - activity, temperature - activity, etc.) and they are all used to learn about various Earth processes.

Temperature-Composition Diagrams. This laboratory exercise explores temperature-composition (T-X) phase diagrams. Figure 2a shows a typical phase diagram that describes the melting relations in the **chemical system** A - B. Temperature is shown on the vertical axis and composition of all phases are indicated on the horizontal axis. The composition scale is in weight percent ranging from 100% A on the left to 0 % A on the right (the scale could just as easily be reversed with % B increasing to the right). The composition of all solids that may exist in this chemical system can be described by reading the scale on the horizontal axis. This hypothetical chemical system, A - B contains three solids (phases) at low temperature: A, B and C. The composition of solids A, B and C are 100% A, 25% A and 0% A, respectively. T_{mA} and T_{mB} represent the **melting temperature** of each of compounds A and B, respectively. The melting point of a compound is a diagnostic characteristic such as specific gravity or hardness and can be used to unambiguously identify a compound. A mixture of the two compounds will begin to melt at the **eutectic** temperature, a temperature lower than the melting temperature of either compound alone. The eutectic temperature is a diagnostic characteristic of a chemical system (more than one compound). Given a eutectic temperature measurement it is possible to identify uniquely the chemical system (Table 1). For a fixed composition, such as **R** (Fig 2a), the temperature above which no solid remains is given by the **liquidus** (or saturation) curve. Above the saturation curve there will be no crystals because they all melt. At temperatures below the eutectic temperature only solid is present. Between the eutectic temperature and temperature given by the liquidus curve (for any specific composition) some material will be present as crystals and some as liquid (**2-phase field**). At a given temperature, such as T_1 it is possible to determine the proportions of solid and liquid (crystals and fluid). The horizontal line segment (**tie line** XZ at temperature, T_1) connects the composition of the solid on the left with the composition of the coexisting liquid on the liquidus curve. The tie line, XZ, can be divided into two shorter line segments XY and YZ. The proportion of liquid is given as the ratio of XY/XZ. The proportion of solid is given by the ratio of YZ/XZ. This is the **lever rule** (Brady and Stout, 1980). In the experiments described below the lever rule will be used to construct the liquidus curve from observed solid / liquid ratios.

Real T-X diagrams The phase diagram for ice-halite (H_2O - NaCl; Fig 2b) which is relevant to hydrologic applications closely resembles Fig 2a. Six phases are possible in this system -- The minerals ice, hydrohalite, and halite, and the liquids water (pure H_2O), NaCl liquid (not shown on diagram because it occurs above 40°C), and brine (H_2O - NaCl fluid). This phase diagram can tell us several important things. Here are some examples: (1) The melting point of ice is 0°C exactly. (2) The north polar ice cap must be pure ice with no salt (except in fluid inclusions) in spite of forming from seawater (ice has no solid solution with NaCl)! (3) Once the temperature drops below -20.8°C, it will do no good to salt the roads in order to melt the snow. (4) If a solution at room temperature contains salt crystals, then the salinity of the liquid must exceed 26.3 percent by

Figure 2a. Schematic temperature - composition (T-X) phase diagram. At temperature T_1 , the ratio of liquid to solid is given by the linear measures: XY/YZ . The fraction of the total that is liquid is $XY/(XY+YZ)$ or XY/XZ . Note that as temperature increases from T_1 line segment XY decreases in length indicating that the amount of solid decreases!

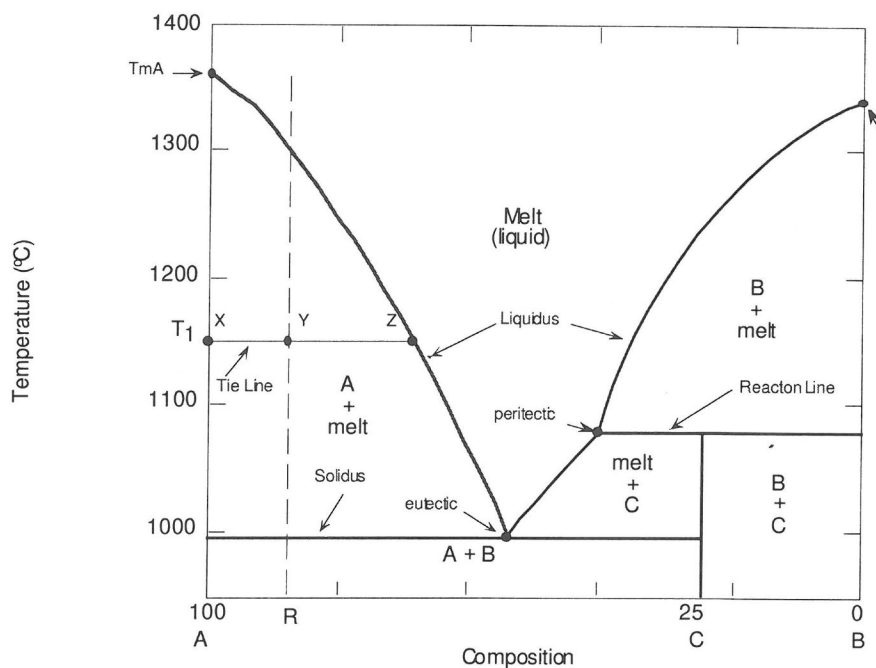


Figure 2b. The Ice - Halite System. The term liquid refers to brine (salt water). Modified from Crawford (1981).

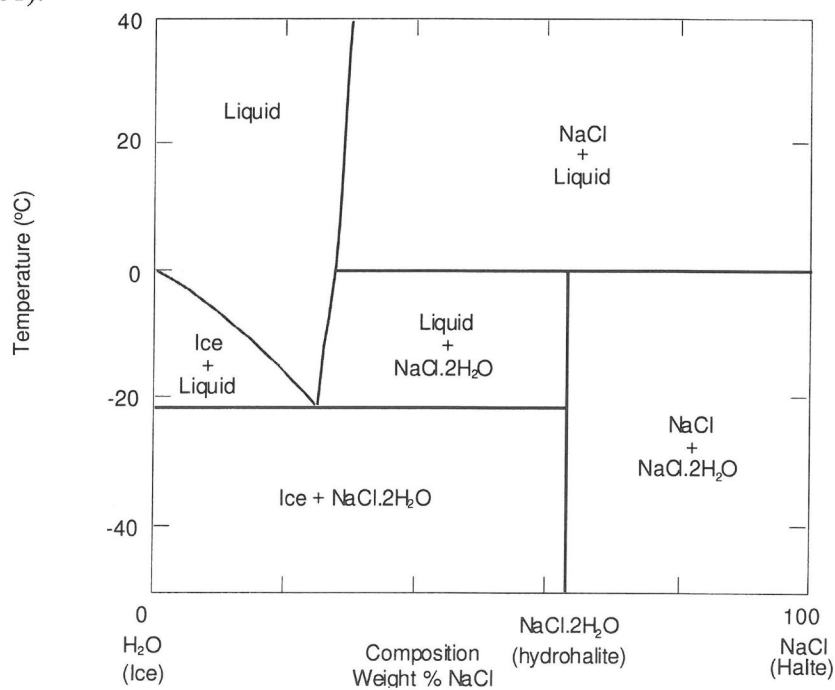
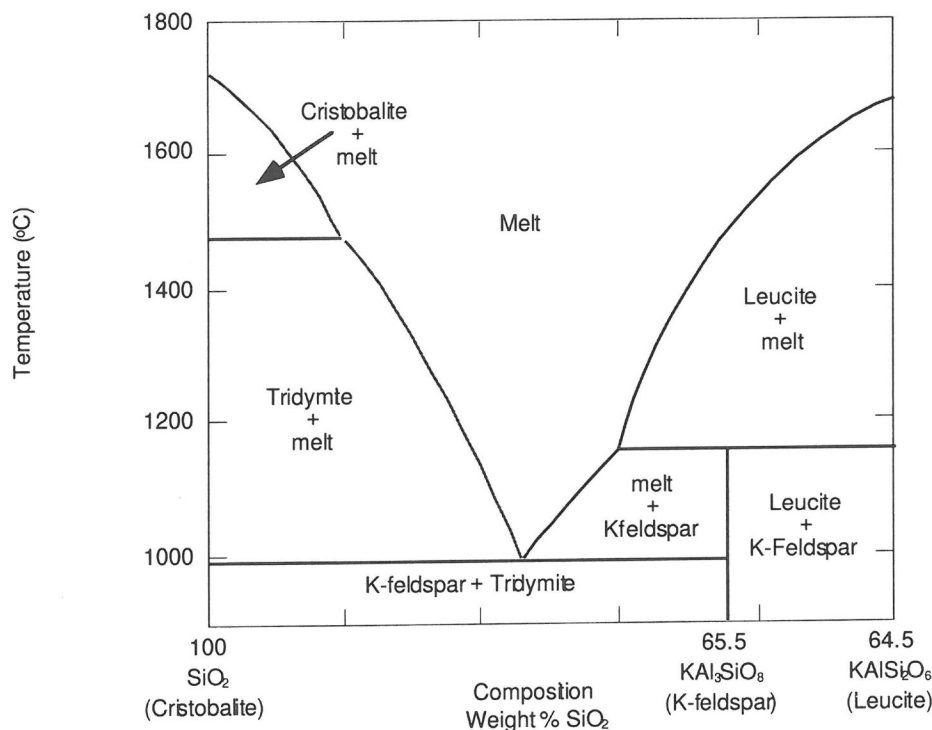


Figure 2c. The Leucite - Silica System. The composition scale is in weight percent SiO_2 . Note that the composition scale is truncated on the right). Redrawn from Schairer and Bowen, (1947).



weight. Such salty fluids are found in the Great Salt Lake and develop during the late stages of crystallization of igneous intrusions. (5) If a mineral contains a fluid inclusion in which the contained aqueous fluid has a eutectic temperature of -20.8°C and a final melting temperature of -4°C , then the fluid must have a salinity of approximately 3.5 weight percent NaCl . Seawater is such a fluid. Perhaps, the mineral precipitated from seawater! Many more things can be learned from this phase diagram, but this will suffice for now. Demonstrate to your instructor your understanding of phase diagrams by showing how each of the above real life applications can be deduced by inspection of Figure 2b!

The leucite - silica (KAlSi_3O_8 - SiO_2) system is relevant to study of the origin of certain igneous rocks, and the phase diagram closely resembles the ice-halite phase diagram (Fig 2c). The leucite - silica diagram tells us several things also: (1) Five phases are possible: the four minerals leucite, k-feldspar, cristobalite (quartz polymorph), tridymite (quartz polymorph), and melt of compositions ranging from KAlSi_3O_8 to SiO_2 . (2) The melting point of cristobalite and leucite (what are they?). (3) K-feldspar does not melt to a liquid of its own composition (it transforms to yield some melt and another mineral -- **incongruent** melting). (4) You will never find leucite and quartz in the same rock under equilibrium conditions -- a reaction will take place to form orthoclase under equilibrium conditions. (5) The vertical boundary at 65.5 weight percent SiO_2 is a fundamental dividing line in this simplified chemical system. Rocks containing greater than 65.5% SiO_2 will contain quartz whereas rocks containing less than 65.5 % SiO_2 will not contain quartz-- a first order observation when you are trying to name a rock on the basis of its mineralogy!

The phase diagrams shown in Figures 2b and 2c are the result of considerable efforts by several experimentalists.

Table 1. Selected phase data for aqueous solutions of chloride species commonly found in fluid inclusions (from Crawford, 1981)

Dissolved Species	Eutectic T (°C)	Eutectic composition (wt.%)	Solid Phases	Solid Phases	Optical Properties	Solid Melting Relations
			H ₂ O	ice	hexagonal, colorless RI ϵ 1.313 ω 1.309	0 °C, congruent
NaCl	-20.8	23.3% NaCl	NaCl·2H ₂ O	hydrohalite	monoclinic	+0.1°C, incongruent
			NaCl	halite	cubic colorless RI 1.544	
KCl	-10.6	23.3% KCl	KCl	sylvite	cubic colorless yellowish RI 1.490	
CaCl ₂	-49.8	23.3% CaCl ₂	CaCl ₂ ·6H ₂ O	antarticite	hexagonal colorless RI ϵ 1.393 ω 1.417	30.08 °C, incongruent
MgCl ₂	-33.6	23.3% MgCl ₂	MgCl ₂ ·12H ₂ O			-16.4 °C, congruent
NaCl-KCl	-22.9	23.3% NaCl 23.3% KCl				
NaCl-CaCl ₂	-52.0	1.8% NaCl 29.4% CaCl ₂				
NaCl-MgCl ₂	-35.0	1.56% NaCl 22.75% MgCl ₂				

The Experiments

A portion of the phase diagram for the X - Y chemical system will be investigated by performing three heating and cooling experiments, A, B and C. Compound X is an unknown liquid at room temperature and compound Y is some unknown solid at room temperature). Small experimental capsules (either sealed transparent capillary tubes or synthetic quartz) containing random amounts of X and Y have been prepared. These samples were placed in an oven (the sample chamber of a Heating/Freezing stage) whose temperature could be precisely controlled and monitored ($\pm 0.05^\circ\text{C}$). The transparent nature of the experimental capsules permits direct observation of the contents during the experiment. As the temperature is alternately lowered and raised, changes take place (phase transitions-- melting, chemical reactions). Record the temperature at which phase transitions occur and note the identity of all phases present below and above the phase transition temperature for each reaction vessel. The instructor will lead you through a video recording of the experiments or show you a series of still frames that illustrate the progress of the experiment (experiment C only). You will make observations and collect requested data (see below).

EXPERIMENTS

In this exercise you will collect real data and construct a real phase diagram, and to add a bit of drama, even discover the identity of the chemical system you are dealing with. View the video of the three experimental runs. Answer the questions pertaining to each experiment at the conclusion of each experiment.

Experiment A

The experimental capsule is cooled until everything is solid (below -80°C) and then warmed slowly until the contents is entirely liquid. Describe what happens in detail.

Experiment B

The experimental capsule is cooled until everything is solid (below -80°C) and then warmed slowly until the contents is entirely liquid. Describe in detail what happens.

Experiment C

In this experiment we will make a sketch of the experimental capsule and measure the areas of the solid and of the liquid at various temperatures. The experimental capsule is cooled until everything is solid (below -80°C) and then warmed slowly until the contents are entirely liquid. At various temperatures we will make a quick sketch of the experimental capsule by placing a transparency on the TV screen and outlining the experimental capsule, the solid crystals and the gas bubble (think about how can the area of the liquid could be determined). There will be one sketch for each temperature. Each sketch will be distributed to a different student or group of students who will be responsible for determining the area of the inclusion (experimental vessel), the volume of the vapor bubble, and the volume of solid. This constitutes one data set. The area will be determined by placing the transparency on a sheet of graph paper and counting squares. Because the shapes are round, you may want to keep track of partial squares to get a more accurate count. Each student or group will be responsible for the data set corresponding their assigned temperature. When each student or group has finished making the area determinations for their temperature, the data will be tabulated on the board for everyone to record (Each student or group will supply values for one row-- Columns A-D; Figure 3). Be sure to record the temperature at which melting begins as accurately as possible.

From the area measurements we will determine the volume of the liquid, the fractions of liquid, and the salinity of the liquid at each temperature. The liquidus is plotted from the paired temperature - liquid salinity data (See next section).

QUESTIONS

Experiment A

- What type of melting behavior is exhibited by the contents of A (congruent or incongruent)?
- Based on your observations what must be in experimental capsule A (Refer to Table 1)?

Experiment B

- The melting behavior in *Experiment B* indicates that the experimental capsule contains at least two substances. The eutectic temperature can be used to uniquely characterize the chemical system for a mixture of two or more substances. What must be in capsule B (Refer to Table 1)?
- What factors might influence the accuracy of the eutectic temperature measurement? How precise do you think the measurement is?
- Potter (1978) in a series of experiments measured the “freezing point depression” of an aqueous fluid as a function of increasing amounts of various dissolved substances. He derived the equation below for your chemical system.

$$T = -0.581855*W - 0.00348896*W^2 - 0.0004314*W^3$$

$$W = -1.76958*T - 0.042384*T^2 - 0.00052778*T^3$$

where T = the final melting or liquidus temperature ($0 < T < -20.8^\circ\text{C}$)
and W = the final weight percent salt in the solution ($0 < W < 23$ NaCl wt % equiv.)

* What is the salinity of the fluid in capsule B?

Experiment C

- What substances does experimental vessel C contain?
- What is the salinity of the solution?
- The data in columns A- D can be used to experimentally determine the solvus in this system. To do this you need to first calculate the necessary values for columns E to G.

<u>Column</u>	<u>Header</u>	<u>Explanation</u>
A	Temperature	Temperature in $^\circ\text{C}$
B	Capsule area	Size of experimental vessel (area measurement in arbitrary squares)
C	Bubble area	Amount of bubble (area measurement in arbitrary squares)
D	Solid area	Amount of solid (area measurement in arbitrary squares)
E	Liquid area	Amount of liquid (area measurement in arbitrary squares)
F	XI	Liquid as fraction of total solid and liquid (ratio)
G	Liquidus	Wt. % NaCl Equiv. at temperature*

*At any given temperature a tie line (XZ in Fig. 2a) pairs the composition the solid with that of the liquid. The tie line XZ consists of the sum of the shorter segments XY and YZ, which represent the relative amounts of liquid and solid, respectively. Since the length of XY as a fraction of XZ is known (Col. F) the length of XZ can be determined if we know the absolute length of XY in units of weight percent ($XZ = \text{fraction liquid} / XY$). How can we determine the absolute length of XY in units of weight percent? One could do two experiments in which the freezing point of water is determined one that yields a temperature slightly higher and one that yields a temperature slightly

lower than the one observed in our experiment. In our case we will simply use Potters equation to calculate the salinity of a fluid with a freezing point depression equal to the one we observed (see b above!). This salinity represents XY.

- d) In a few paragraphs discuss your results. Be sure to plot your data on a graph that shows composition (NaCl El. Wt. % Equiv.) along the abscissa and temperature ($T^{\circ}\text{C}$) along the ordinate (Column A vs G). Plot the equation of Potter (1978) on the same graph. State and discuss assumptions, limitations, areas of agreement, areas of disagreement.

Figure 3. Sample Data Table

A	B	C	D	E	F	G
Temper- ature	Capsule Area	Bubble Area	Solid Area	Liquid Area	Xl	Liquidus

Columns A - D are for data; Columns E - G are for calculated values

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PHASE DIAGRAMS IN VIVO

Information for the Instructor

INTRODUCTION

The topic of phase diagrams in many mineralogy texts begins with an introduction to temperature-composition (T-X) diagrams (e.g. Klein and Hurlbut, 1993). Commonly the instructor is faced with introducing a plethora of terms (tie lines, joins, reaction lines, liquidus, solidus, melting point, incongruent, congruent melting, peritectic, eutectic, phase, equilibrium, disequilibrium, 1 and 2 phase fields) and explaining their meaning and significance to a by now bewildered audience. When students are able to visualize a phase diagram in action or even be engaged in creating one from their own experimental data, the vocabulary and concepts become intuitively clear. Fluid inclusions, which occur naturally in all minerals, are ideal experimental vessels that permit the acquisition of temperature - composition data for the construction of T-X phase diagrams. Fluid inclusions are particularly suitable because they bridge the gap between experimental petrology (mineral assemblages) and the minerals themselves (i.e. they give information on the conditions of formation of the minerals that contain them)!

This lab has been run using various formats depending on class size, time constraints, available equipment, and objectives of the instructor. If the class size is small, sufficient time is available and a fluid inclusion stage is available the entire class may visit the fluid inclusion laboratory to collect data in real time. For a large class or if a fluid inclusion laboratory is not available a video showing a laboratory tour and the experimental runs is used. Videos of the experimental runs were made by mounting a camera on a microscope and filming the changing proportions of solid (ice) and liquid (brine) in a synthetic fluid inclusion (in quartz) as it was cooled and heated in a FLUID INC. freezing / heating stage. A copy of this video can be obtained from the author by trade of a blank VHS cassette. A collection of still images from the video is also available and can be used in place of the video.

These images are available over the Internet at

<http://www.mines.utah.edu/~wmep/workshop/filab.html>

They can be used by individual students or as a group exercise for the entire class.

This exercise can be done as a homework assignment, although much of the value that the instructor can add would then be lost.

Three experiments have been videotaped. The first two are largely demonstrations, whereas students actively participate in the third experiment. The first experiment shows congruent melting of a substance at precisely 0°C. Students conclude that the substance in the experimental vessel must be pure H₂O as it is the only known substance showing this diagnostic behavior.

The second experiment demonstrates the reality of a eutectic point in a binary system, the significance of the eutectic point in characterizing the chemical system under investigation, and the fact that mixtures melt over a temperature range. This introduces the concepts of tie-lines, the lever rule, "freezing point depression", solid solution, and 1, 2 and 3 phase fields. Applications to everyday life (salting roads in winter) and magmatic systems are easy to point out.

The third experiment is the longest and most interesting. This experiment is essentially the same as the second except that we pause at various temperatures to make sketches to quantify the changing proportions of liquid and solid as temperature is raised. Although the required calculations can be done for each temperature individually on a calculator, it is useful to have the student carry out the calculation in a spreadsheet. Once the spreadsheet is constructed, graphing the results is straightforward. Errors and assumptions are easy to test. The final wrap-up can take one of two forms; an individual report to be turned in at a future time or an immediate group summary and discussion. If an overhead projection system is available for a lab computer the instructor can lead the discussion by suitably manipulating the data in real time to illustrate the discussion.

The purpose of this laboratory as designed is to gain familiarity with simple phase diagrams, their construction, and their applications to the understanding of geological and environmental problems. Subsidiary objectives include development of strategies for data processing including evaluation of assumptions and sources of errors, as well as honing of computer, spreadsheet, presentation (tabular and graphical), and report writing skills. This laboratory develops, reviews or makes use of the following concepts and/or skills.

EXAMPLES AND SOLUTIONS

Several questions are posed throughout the exercise. Suggested answers are provided below along with a real sample data collected during Fall quarter 1996 at the University of Utah (GG 308 Mineralogy).

Figure 1.

- Q.** What must the volume of the bubble be if the density of the vapor is 0.01 gm/cm^3 ?
- A.** At 250°C density = 0.8 gm/cm^3 (given). Assume a volume of 1 cm^3 . The mass of the fluid is therefore 0.8 gm . At 25°C the mass of the water and vapor together is 0.8 gm . The overall density must remain the same if the integrity of the fluid inclusion has not been violated. Furthermore, $V_f = 1 - V_v$. Therefore, $1.0 \cdot V_f + 0.01 \cdot V_v = 0.8$, $1.0 \cdot (1 - V_v) + 0.01 V_v = 0.8$, $1.0 - 1 \cdot V_v + 0.01 V_v = 0.8$, $-0.99 \cdot V_v = -0.2$, $V_v = 0.2$ or about 20% of the volume of the inclusion!

Experiment A

The experimental capsule is cooled until everything is solid (below -80°C) and then warmed slowly until the contents is entirely liquid. Describe what happens in detail.

Liquid persists until the temperature drops below approximately -37°C . At that temperature the fluid turns into a very fine-grained solid. In this case the solid takes up more volume than the same mass of fluid and the bubble collapses a small but noticeable amount. Upon heating the solid recrystallizes to form a large clear crystal. As the melting temperature is approached noticeable changes in the morphology of the solid are seen. Melting takes place instantaneously at 0°C .

Qa. What type of melting behavior is exhibited by the contents of A (congruent or incongruent)?

Aa. *Congruent. Instantaneous melting at 0°C .*

Qb. Based on your observations what must be in experimental capsule A (Refer to Table 1)?

Ab. *The substance in capsule A must be pure H_2O (ice) as this is the only substance that has a melting point of 0°C .*

Experiment B

The experimental capsule is cooled until everything is solid (below -80°C) and then warmed slowly until the contents is entirely liquid. Describe in detail what happens.

Liquid persists until the temperature drops below approximately -37°C . At that temperature the fluid turns into a very fine-grained dark solid. In this case also, the solid takes up more volume than the same mass of fluid and the bubble collapses a small but noticeable amount. Upon heating the solid recrystallizes to form a large clear crystal. At about -20°C the solid begins to break up and liquid is visible. By -6.6°C all the solid has melted.

Qa. The melting behavior in *Experiment B* indicates that at the experimental capsule contains at least two substances. The eutectic temperature can be used to uniquely characterize the

chemical system for a mixture of two or more substances. What must be in capsule B (Refer to Table 1)?

Aa. *Capsule B contains H_2O and $NaCl$. The eutectic temperature observed near $-20^\circ C$ rules out the presence of KCl alone. Solution of H_2O and $CaCl_2$, $MgCl_2$, $NaCl-KCl$, $NaCl-CaCl_2$ and $NaCl-MgCl_2$ all have eutectic temperatures well below $-20^\circ C$.*

Qb. What factors might influence the accuracy of the eutectic temperature measurement? How precise do you think the measurement is?

Ab. *Several factors can potentially influence the accuracy and precision of the eutectic temperature measurement. Instrumentals factors: Rapid heating may register a temperature that is higher than actually present at the site of melting (disequilibrium). Observational: Ice float and because we are looking "down" the ice obstructs our view of any liquid that may be forming "below" it; The first "droplets" of liquid are likely to wet the solid and thus be difficult to discern; In dilute solutions the index of refraction of the liquid may be very similar to that of the solid making small amounts of liquid difficult to detect; In dilute solutions very, very small amounts of liquid will be produced initially (see Figure 2a).*

Qc. What is the salinity of the fluid in capsule B.

Ac. Use the relationship: $W = -1.76958 \cdot T - 0.042384 \cdot T^2 - 0.00052778 \cdot T^3$, where T = the final melting or liquidus temperature ($0 < T < -20.8^\circ C$). For $T = -6.6^\circ C$, $W = 10.0$ wt % $NaCl$ equivalent.

Experiment C

In this experiment we make a series of sketches on sheets of overhead transparencies of the fluid inclusion as viewed on the monitor at various temperatures. The areas of the inclusion, contained solid, and bubble are determined by placing the transparency on a sheet of graph paper and counting squares (The area of the inclusion only needs to be sketched once because it does not change). The area of the liquid is obtained by subtracting the area of the bubble and the solid from the area of the inclusion. Applying the lever rule the locus of the liquidus can be calculated provided an absolute starting point is given. That starting point is the salinity of a solution whose freezing point depression is $-6.6^\circ C$.

Qa. What substances does experimental vessel C contain?

Aa. *Same answer as Experiment B.*

Qb. What is the salinity of the solution?

Ab. *Same answer as Experiment B.*

REQUIRED MATERIALS

- Video of a laboratory tour and an experimental run. Alternatively, still images of the experiment as it proceeds. Experiment A cannot be done with still images alone. The same images used in Experiment C can be used for Experiment B. The lab description assumes that a video or stills are being used in the lab.
- TV monitor/VCR to play back video recording of experimental run or for live data collection.
- Overhead transparencies, marker pen, and graph paper for quick area determinations.

ACKNOWLEDGMENTS

The exercise was considerably improved by the comments of John Brady, Dexter Perkins, Andy Campbell, Marlene McCauley. Feedback from the attendees of the Mineralogy Workshop was much appreciated.

Figure 3. Sample Data Table (Columns A - D are for data; Columns E - G are for calculated values) The values in columns B, C and D are area measurements (squares on a sheet of graph paper. The absolute values depend on the size of the squares and also on the size of the image on the monitor! The calculations for columns E - G are explained in the student hand out.

A	B	C	D	E	F	G
	1257					-6.6
Temper - ature	Capsule Area.	Bubble Area	Solid Area	Brine Area	XBrine	Liquidus
-18.0	1257	239	553	465	0.46	21.9
-17.0	1257	248	494	515	0.51	19.6
-16.0	1257	251	505	501	0.50	20.0
-14.0	1257	264	428	565	0.57	17.5
-13.0	1257	273	412	572	0.58	17.2
-12.0	1257	263	382	612	0.62	16.2
-11.0	1257	277	345	635	0.65	15.4
-10.0	1257	295	298	664	0.69	14.5
-9.0	1257	290	197	770	0.80	12.5
-8.0	1257	276	133	848	0.86	11.6
-7.5	1257	293	53	911	0.95	10.6
-7.0	1257	311	11	935	0.99	10.1
-6.6	1257	322	0	935	1.00	10.0
Salinity	Temp					
10.0	-6.6					

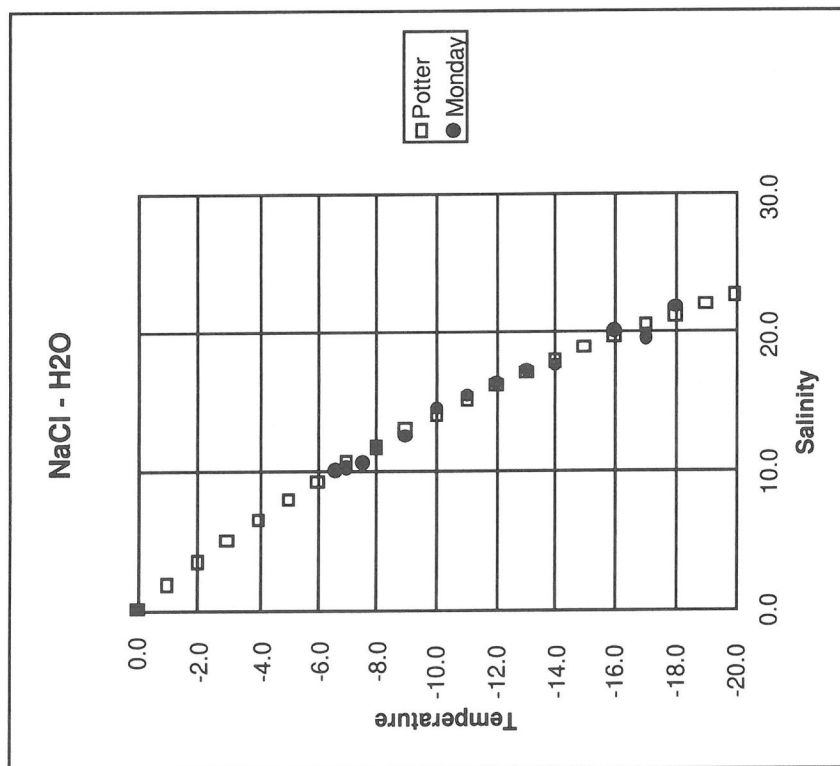


Figure 4. Temperature (A) vs Liquidus composition (G)

EXPERIMENTS ON SIMPLE BINARY MINERAL SYSTEMS

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This exercise is devised to simulate a series of experimental runs in which binary mineral mixtures are melted using very high-temperature furnaces in order to determine the characteristics of mineral systems and igneous melts. Of course, natural melts are far more complex in composition, but it is surprising how much one can learn from simplified analog systems. In an experimental laboratory you begin a study by preparing mixtures of two minerals in various proportions. The minerals are ground finely and placed in a platinum crucible. Platinum (or gold) is used because of its high melting temperature and lack of contamination of the “charge” (as the sample is commonly called). The crucible is placed in the furnace and held at a specified temperature for several hours. When the “run” is over, the charge is *quickly* removed from the furnace and rapidly cooled in a stream of compressed air or occasionally in water. Any melt that may have been produced will solidify immediately as *glass*. Any minerals that may have been stable at the run temperature, will be present as crystals, either recrystallized in the solid state below the melting temperature, or imbedded in glass if some melting occurred. Several runs are repeated, using various proportions of the two starting minerals defining the system over a range of temperatures. It is also possible to determine the composition of the run products (both glass and crystalline) by cutting the charge, making a thin section, polishing the surface, and analyzing the constituents with an electron microprobe.

Using data from a series of experiments, including: 1) initial mixture composition, 2) the run temperature, 3) the phases present in the resulting charge, and 4) the composition of each phase, a **phase diagram** can be constructed. There are several types of phase diagrams, but the most common is a careful plot of temperature versus composition (a “T-X” diagram) for all phases present at equilibrium in the run products (either solid or glass/liquid) for a particular temperature.

Since many schools lack proper furnaces, and you can get a very nasty burn anyway, we will use a computer to simulate the process. The simulation is a program called MinExp, that is on the PC's in the computer lab. You will be able to perform experimental runs for 2 different mineral systems; start with “Experiment 1.” You begin the exercise by choosing the initial mineral proportions of two (unknown) minerals in a mixture. The computer crucible will handle about 1 gram of sample, so try to make your weight totals nearly equal to that number. Next pick a run temperature (between 1000°C and 1700°C should be adequate). When the run is “complete” observe the graphical representation of the crucible. The colors will represent specific phases, either a certain mineral or glass, and their approximate relative amounts. This data may be useful to you for determining your next experimental run. The computer will allow you unlimited experimental runs, an advantage not enjoyed by the experimental petrologist who must invest time and money to perform the real thing. You should do fine with 30 or so runs for each system, spread over the complete compositional range, including the pure end-members. You may quit at any time and resume later if you care to digest initial results before proceeding.

You can also analyze your run products with a mock electron microprobe, an x-ray spectroscopic instrument. This will produce a chemical analysis of each physically distinct phase in the experimental run products (crystals, or glass). Microprobes provide data with a modest degree of statistical uncertainty. Thus your analysis, typically given as weight % oxide constituents, will

probably not sum exactly to 100%. Acceptable analyses generally range between 98-102% (2% relative error). Remember that the number of components in the phase rule is the *minimum* number of chemical constituents required to comprise the various phases in the system. Our binary systems ($C = 2$) are mixtures of complex mineral end-members that each contain more than one oxide. Thus you should not confuse the number of oxides with the number of components. The microprobe results include a calculation of the weight fraction (X_2) directly from the chemical data. The clever student might guess the identities of the (common) minerals involved by noting the oxides present and their relative proportions. Use of a mineral formula calculation would help convert the oxide analyses to a mineral formula to confirm any guesses.

When you finish, plot a phase diagram for each system on graph paper with temperature as the ordinate (y-axis) and composition as the abscissa (x-axis). Composition may be expressed as $X_2 = n_2/(n_1 + n_2)$, where n_1 and n_2 are the number of grams of minerals 1 and 2, respectively. Since $(n_1 + n_2)$ is the total number of grams, X_2 is commonly called the **weight fraction** of component 2. If we measured n_1 and n_2 in moles, X_2 would be the *mole* fraction. We will use weight fractions here. Of course, in binary mixtures $X_1 = 1 - X_2$. For your plots, the abscissa will thus run from a value of zero (pure component #1) on the left to one (pure component #2) on the right.

For each temperature of your results, plot the composition of *each phase*, crystal or glass (=melt), that occurs in the run at that temperature. Be sure to label what each phase is as you do this (maybe use a color or symbol code). You may discover that two or more phases coexist at equilibrium under some conditions, and that such occurrences are worth searching for and concentrating in your graphs. Indeed, once you get used to the patterns, you may elect to concentrate exclusively on runs with more than one phase. Once all of your data are plotted, connect all of the points for any single phase *that coexists with any specific other phase(s)* with a solid line. In other words, draw a line through all of the points representing liquid compositions that coexist with a particular solid, and all points for solid compositions that coexist with a liquid or another solid. The connected points should produce a smooth curve for each phase. The **liquidus** is defined as the curve representing the composition of the liquid that coexists with a solid phase. If solid solution is possible, there may also be a **solidus**, which is the curve representing the composition of the solid that coexists with a liquid. These curves separate the diagram into fields. When a diagram is complete, you should be able to place your pencil point at any point on the diagram, and predict what phase or phases are stable under those T-X conditions. Label each field with a label that describes the phase or phases that would be present if your experiment were conducted at the T and X conditions appropriate to that field. You may want to use a spreadsheet to record and plot your data.

It is possible to run Excel in one window and the program in another, or use two adjacent computers. Plotting multiple points in Excel for a single temperature is a problem for most students, and it may take you some time to figure out how to do this. If you are not yet comfortable with Excel, you may want to do this one by hand. If you do use a spreadsheet, use small symbols, and make sure those representing one phase are quite distinct from those representing another.

Next look at the various fields on your diagram. Briefly write at the bottom of the diagram for each field whether the composition of any phases are temperature dependent. In other words, would the composition of a phase shift if the temperature were raised or lowered slightly? We will discuss the results in class, so make photocopies to hand in, and keep the originals for your use in class.

Experiments on Simple Binary Mineral Systems

NOTES TO THE INSTRUCTOR

Many students wonder how phase diagrams are determined. Most of them have the initial idea that phase diagrams are ordained by some diabolic scientific deity. I have always wanted my classes to understand that the results are strictly empirical, and are interpretations of experiments. No matter how often I tell them this, they really don't get it. So I decided to let them determine a diagram themselves. We don't have any furnaces at Whitman for doing this, and the prospect of major burns was a further deterrent, so I decided to program a computer simulation of the process. This way students can make many experimental runs quite rapidly. I chose the eutectic Di-An system and the Ab-An solid solution.

This program is a Visual Basic program that should work on any PC running Windows95. It is available from the Whitman College Anonymous FTP site:

marcus.whitman.edu

Username: **anonymous**

Password: **your_email_address**

When you are on the Whitman Server, change directories to:

pub\winter

and download the file Minexp.exe.

Minexp.exe is a self-extracting file that include the program MinExp and necessary data files. Copy it to an empty directory that you name as you choose and run it (usually by double-clicking it in Explorer) to extract the appropriate files. There are a few dynamic link library files (DLL extensions) that are fine in the same directory as the program. You may prefer to put them in your WINDOWS\SYSTEM directory instead, where they will be available to other programs that may require them in the future.

If there are any changes, you may find a note about it on my web page:

<http://www.whitman.edu/Departments/Geology/WinterBio.html>

You may also address any comments to me at: winterj@whitman.edu.

A sample screen image follows. It shows choices of 0.2 grams of mineral one mixed with 0.8 grams of mineral 2 run at 1470°C. The microprobe results are shown in a window. All a student need do is plot T vs. X_2 for each phase.

Experiment 1

Enter number of grams of mineral 1

Enter number of grams of mineral 2

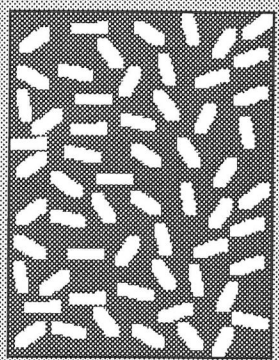
Enter Temperature in Celsius

Begin the Run

Menu

Microprobe the Phases

Charge



glass

crystals

Microprobe Results

Temperature = 1470 degrees Celsius

	glass	crystal
SiO2	46.27	43.26
Al2O3	27.65	36.61
MgO	04.51	00.08
CaO	21.50	20.06
Total	99.93	100.01
X(2)	0.75	1.00

COMPUTER GENERATED CRYSTALS USING *SHAPE*

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The software package known as SHAPE (Shape Software 521 Hidden Valley Road, Kingsport, TN 37663) provides an excellent method for accurately drawing crystals. The following three boxes describe the basic steps involved in using SHAPE. Refer to these instructions when completing the exercises.

GETTING STARTED

The program will be loaded into the computer for you. You may have to activate the program by clicking twice on the crystal icon entitled SHAPE 4.2. When everything is ready a screen headed by

◇>CRYSTALLOGRAPHIC DATA FOR CRYSTAL 1< ◇

will appear on the screen. You are now ready to begin.

ENTERING THE CRYSTALLOGRAPHIC DATA

Selecting Crystal Class and Cell Parameters

All 32 crystal classes are listed (by crystal system) on this first screen. The computer automatically selects m3m (short for $4/m\bar{3}2/m$) under the ISOMETRIC heading.

If you choose any isometric class, and activate the OK button, the computer will automatically enter unit cell dimensions (all 1.0) and inter-axial angles (all 90.0°) and display a new screen.

If you choose any non-isometric class the computer will request the necessary "parameters" (unit cell dimensions and inter-axial angles) in boxes at the screen bottom. Note that SHAPE automatically adds fixed dimensions or angles for you. After the appropriate parameters are entered activate the OK button. A new screen will appear headed:

◇>FORMS 1 TO 20 FOR CRYSTAL 1< ◇

Entering Miller Indices and Central Distances

This second screen allows you to enter the Miller indices of each form you choose to draw on the crystal. Three indices must be entered (one each for H, K, & L) for each form. In addition, the central distance (relative distance from crystal's center to face) must be entered for each form on the drawing. Enter each index in the appropriate box provided, i.e. 1 0 0. The fourth box (headed "Dist") is for the central distance (CD).

Note, SHAPE automatically enters CD =1 for each form; if some other value is desired it must replace the one. After all four numbers are entered, press the "return" key. You will immediately see a prompt asking for indices and CD of the second form. You may enter as many additional forms (up to 20) as you desire. After all the forms and CD's are entered, select the "DONE" button to exit the form entry cycle. SHAPE will then draw the crystal.

MODIFYING CRYSTAL DRAWINGS

Adjusting the Size of Faces

This option allows you to increase or decrease the relative size of a form on the crystal. It is activated by selecting the ADJUST FACE SIZE option under the EDIT menu. After the ADJUST FACE SIZE option has been activated select the desired face by placing the cursor on it and clicking the mouse. Face size is adjusted by modifying the CD. This is accomplished with the ↑ and ↓ keys.

- ↓ increases CD, decreases face size
- ↑ decreases CD, increases face size

Faster CD adjustments are made by depressing the Option key (fairly fast) or Shift key (very fast), while using the arrow keys. After adjustments are complete redraw the crystal by selecting "Recalculate Crystal" under the "ADJUST FACE SIZE" menu.

Adding New Form

New forms can be added to your crystal using the following procedure. Select the MODIFY FORM LIST option from the EDIT menu. At the bottom of the screen select NEW FORM, then enter the desired Miller indices and CD. Activate the ACCEPT button to add the new form to your list (you will see the new form added to the bottom of your form list). Click the DONE button to redraw the crystal with the new form.

Removing a Form

To delete a form select MODIFY FORM LIST from the EDIT menu. Select the form you want to remove by clicking the circle in front of the indices. These indices will then appear in the boxes at the screen bottom. Click the REMOVE option then the ACCEPT button and the deletion is complete (indices of the deleted form will disappear from the form list). Click the DONE button to redraw the crystal with the form deleted.

Rotating the Crystal

Orientation of the drawing on the screen can be modified by using the 2, 4, 6, 8, and 5 keys on the numerical pad (right side of keyboard).

Identifying a Face

Miller indices of any face on the crystal can be instantly identified by using the IDENTIFY FACE option under the EXPLORE menu.

Locating a Form

All faces in a chosen form can be easily identified by using the LOCATE FORM option under the EXPLORE menu.

Locating a Face

Any face can be located by using the LOCATE FACE option under the EXPLORE menu.

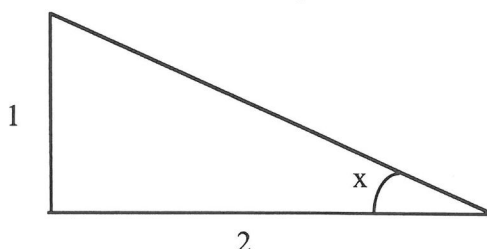
Interfacial Angles

The interfacial angle between any two faces on your crystal can be calculated (if indices of the two faces are known) by using the INTERFACIAL ANGLE option under the EXPLORE menu.

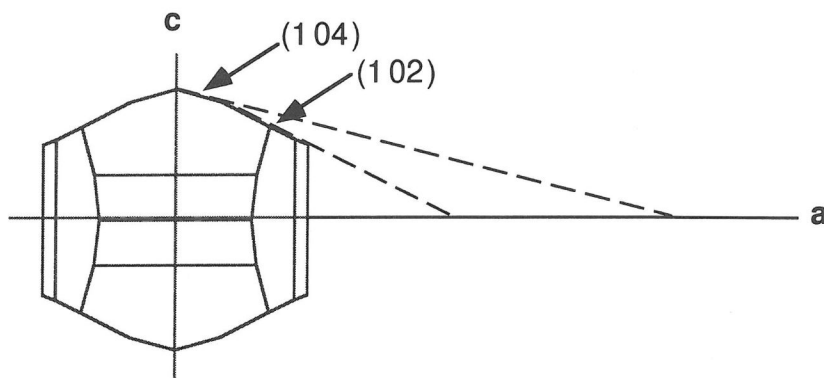
Use the "Interfacial angles" routine to find the interfacial angle $(001) \wedge (102) = \underline{\hspace{2cm}}$. Compare this value with the acute angle "x" shown in the right triangle with sides of one and two (i.e., a face formed by stacking identical cubes in a 2:1 ratio).

$$x = \text{atan}(0.5)$$

use your calculator



Use the "remove a form" routine to delete the cube. Add a second pyritohedron with indices {104} and CD = 1, to your crystal. Is the orientation of (104), relative to (102) consistent with a stacking of 4 units along **a** and 1 on **c**? _____ (the drawing below shows the crystal rotated to provide a side view and the faces extended to intercept the **a**-axis).



Use the "Locating Forms" routine to examine the faces in both $\{102\}$ and $\{104\}$. Can you find face (201) ? If not delete $\{104\}$ and add $\{201\}$ to your form list. What does this result tell you about the forms $\{102\}$ and $\{201\}$ in class $2/m\bar{3}$?

The development of positive $\{101\}^*$ and negative $\{011\}$ rhombohedra often make alpha-quartz (class 32) appear to have 6-fold symmetry. In most cases, however, the two rhombohedra are not equally developed, thereby revealing the true 3-fold symmetry. We can examine this situation using SHAPE. [*Note: for hexagonal and trigonal crystals, which normally have indices $\{hki\}$, SHAPE ignores the "i" index as this value can be calculated from $i = -(h + k)$.]

Select "Begin again" from the EDIT menu; this will rerun SHAPE. Under the TRIGONAL column select 32 (the symmetry of quartz). At the bottom of the screen enter dimensions of the quartz unit cell:

$$a = 4.9 \quad \text{and} \quad b = 5.4$$

Enter the following forms and central distances:

1	0	0	1	(the hexagonal prism)
1	0	1	1	(the positive rhombohedron)
0	1	1	1	(the negative rhombohedron)

Select DONE to exit the form entry loop.

This calculation should produce a "Hexagonal-appearing" quartz crystal.

Locate Forms

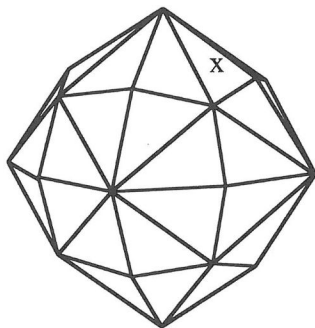
Use the "Locating a Form" routine to determine which faces are in $\{101\}$ and which are in $\{011\}$. Adjust the faces (use Adjust Face procedure) using the following central distances.

(100)	1.0
(101)	1.5
(011)	1.7

Redraw the crystal. Note that the six terminating faces are not related by symmetry (i.e., they do not belong to a single form).

The hexoctahedron

Select "Begin again" from the EDIT menu; this will rerun SHAPE. Under ISOMETRIC select class $m\bar{3}m$ (short for $4/m\bar{3}2/m$) then click the "OK" button. Enter the indices (321) and CD= 1, then press return and DONE. A 48-faced form, called the hexoctahedron will appear. Use the Identify Face option to identify the face marked with an "x" on the hexoctahedron.



The indices of the face "x" are _____

Add a new hexoctahedron with indices (642). Explain what happens and why.

For fun add at least two additional hexoctahedra, each with indices other than 1, 2 or 3, to your crystal.

HOMEWORK PROBLEM

Solve the problems below using SHAPE

1) The study of a particular tetragonal crystal gave the following data:

Form {001} has 2 faces
Form {100} has 4 faces
Form {111} has 4 faces
Form {101} has 8 faces
Form {121} has 8 faces

To which crystal class must this crystal belong? Explain your answer (i.e., how were the other possibilities eliminated?).

2) The study of a particular trigonal crystal revealed that the following forms were present:

Pedion
Hexagonal prism
Ditrigonal prism
Trigonal prism
Trigonal pyramid

To which crystal class must this crystal belong? Explain your answer.

TWINNING EXERCISES

In most cases the relationship between individual domains within a twinned crystal can be described by rotation about a twin axis or reflection across a twin plane. Both of these operations can be performed using SHAPE.

I. Twinning by Reflection

A. The Gypsum Fish-tail Twin

The common "fish-tail" gypsum twin is described as "twinned on (100)." This means that the "fish-tail" contact twins can be generated by reflecting one half of a gypsum crystal across the (100) plane, to generate the twinned crystal. Using SHAPE, this operation is performed as follows:

1. Enter SHAPE: From the start-up screen:

- a. select **2/m** from the monoclinic section
- b. enter unit cell parameters
 $a = 5.68$ $b = 15.5$ $c = 6.29$ $\beta = 113.8$, then click OKAY
- c. enter the following forms and CD's

1	2	0	1.0
0	1	0	0.5
-1	1	1	1.0

then click ACCEPT and DONE

2. To twin the crystal: select the **Twins** option under the **TWINS/EPITAXY** menu.

3. From the dialog box headed **‡ > TWIN MODE < ‡**

- a. choose "contact" and "hide interfacial edges"
- b. select the Okay button

4. From the dialog box headed **‡ > TWIN OPERATOR 1 < ‡**

- a. choose "Reflection on" and enter 1 0 0 as indices of the twin operator
- b. click the ACCEPT button
- c. select the DONE button

5. From the dialog box headed **‡ > COMPOSITION PLANE 1 < ‡**

- a. enter the indices 1 0 0 as the composition plane
- b. click the ACCEPT button
- c. select the DONE button

An inverted "fish-tail" gypsum twin will appear. The twin can be rotated into the standard orientation using buttons on the numeric pad (right end of the keyboard).

B. Staurolite Cruciform Twin

The distinctive staurolite cruciform twin can be formed by reflection across (031). This operation produces twin individuals that are almost, but not precisely, 90° apart. To simplify the drawing of this twin an untwinned staurolite crystal, showing the forms {110}, {010}, {201}, and {001} has been pre-drawn and stored under the file-name "Staurolite." The following steps will produce a staurolite twin.

1. Load the pre-drawn crystal by selecting the "**Get data from a remake file...**" option from the starting SHAPE screen and choosing "Staurolite" from the menu.
2. To twin the crystal: select the **Twins** option from the **TWINS/EPITAXY** menu.
3. From the dialog box headed \ddagger **TWIN MODE** $< \ddagger$
 - a. select: **Interpenetration with intercrystalline edges**
 - b. for the query **Intra-facial edges** select:- hide
 - c. click the Okay button
4. From the dialog box headed \ddagger **TWIN OPERATOR 1** $< \ddagger$
 - a. choose "Reflection" and enter 0 3 1 as indices of the twin plane
 - b. click the ACCEPT and DONE buttons

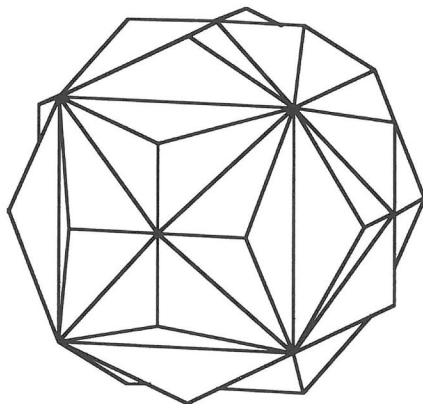
The staurolite twin will appear. The extraneous lines in the drawing can be removed by pressing "Command L" (i.e., the apple button & the "L" key on a Macintosh).

Measure the angle between twin individuals by using the "interfacial angles" routine to find the angle between (001) on crystal one, and (001) on crystal two. Angle = _____

II. Twinning by Rotation

A. The pyrite "iron cross" twin

The iron cross twin (shown below) is a penetration twin formed by a 90° rotation about the c-axis, the [001] direction.



Using SHAPE, this operation is performed as follows:

1. Enter SHAPE:- From the start-up screen:
select **mb3** (short for $2/m\bar{3}$) from the isometric section and click Okay
2. On the data entry screen enter the form $\{102\}$ with CD = 1, select done
3. To twin the crystal: select the **Twins** option under the **TWINS/EPITAXY** menu.

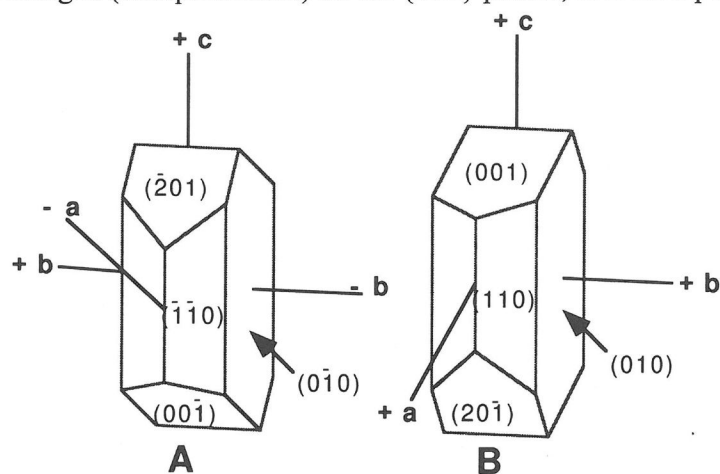
4. From the dialog box headed \ddagger **TWIN MODE** $< \ddagger$
 - a. select: **Interpenetration with intercrystalline edges**
 - b. for the query **Intra-facial edges** select :- hide
 - c. click the Okay button
5. From the dialog box headed \ddagger **TWIN OPERATOR 1** $< \ddagger$
 - a. choose "Rotation" and enter 0 0 1 as indices of the twin axis
 - b. enter a rotation angle of 90°
 - c. click the ACCEPT button
 - d. select the DONE button

SHAPE will then draw the twin. The final drawing can be cleaned up (extra lines removed) by pressing Command L (i.e., the apple button & the "L" key on a Macintosh).

QUESTION: Note that the **c**-axis in pyrite is a 2-fold symmetry axis. Predict what would happen if the angle in step 5. b. were 180° , rather than 90° . Try it to test the accuracy of your prediction.

Carlsbad Twinning on the Computer

Carlsbad twins are penetration twins that commonly form in feldspars. The composition plane is $\{010\}$ and the twin axis is the **c**-axis (i.e., the $[001]$ direction). One twin individual is rotated 180° about the **c**-axis, relative to the other. In the illustrations below note that Fig. A shows how Fig. B would appear if rotated 180° about the **c**-axis. In the twin the two individuals are merged (interpenetrated) on the $\{010\}$ planes, to form a penetration twin.



Drawing the Carlsbad twin is simplified by using a pre-drawn, untwinned monoclinic K-feldspar crystal. This drawing, which has been distorted somewhat to make the twin appear more realistic, is stored under the file-name "Carlsbad." The following steps will produce a Carlsbad twin.

1. Load this pre-drawn crystal by selecting the "Get data from a remake file..." option from the bottom of the starting SHAPE screen and choosing "Carlsbad" from the menu.
2. To twin the crystal: select the **Twins** option from the **TWINS/EPITAXY** menu.

3. From the dialog box headed \ddagger > **TWIN MODE** < \ddagger
 - a. select: **Interpenetration with intercrystalline edges**
 - b. for the query **Intra-facial edges** select:- hide
 - c. click the Okay button

4. From the dialog box headed \ddagger > **TWIN OPERATOR 1** < \ddagger
 - a. choose "Rotation" and enter 0 0 1 as indices of the twin operator
 - b. enter a rotation angle of 180°
 - c. click the ACCEPT button
 - d. select the DONE button

A Carlsbad twin will appear. The extraneous lines in the drawing can be removed by pressing "Command L".

QUESTION: Perform the Carlsbad procedure again, but this time substitute the b-axis [010] in place of [001]. Explain your result.

For fun generate the penetration twin formed when the form {211} in class 23, it twinned by a 90° rotation of the c-axis.

NOTE TO INSTRUCTORS

This package contains two computer exercises that use SHAPE software to teach certain aspects of crystal morphology and twinning. Both exercises are designed to be self-contained; that is, once students become familiar with the computer and software, they can work through the material individually. It is intended that each student will have access to an individual computer.

SHAPE is a software package developed by Eric Dowty. It is commercially available from: Shape Software 521 Hidden Valley Road, Kingsport, TN 37663. Phone (615) 239-3258. Demo versions are available for both PC and Mac computers.

It is assumed that students performing these exercises have been introduced to the basic elements of symmetry, Miller indices, and crystal forms. "Exercises with Computer Generated Crystals" uses SHAPE to explore these concepts in an interactive computer format. The second package, "Twinning Exercises", allows students to draw reflection and rotation twins. Both exercises encourage experimentation and are aimed at students with modest mathematical backgrounds.

The twinning exercises call for previously saved crystal drawings in "Remake Files" named "Staurolite" and "Carlsbad." The staurolite file can be created with the following data:

Crystal Class: 2/m	{0 0 1}	1.7
a = 7.83	{1 1 0}	0.5
b = 16.62	{0 1 0}	0.7
c = 5.65	{2 0 1}	1.3
$\beta = 90^\circ$	{-2 0 1}	1.3

The carlsbad file can be created with the following data:

Crystal Class: 2	{0 0 1}	1.6
a = 8.5	{1 1 0}	1.0
b = 13.0	{1 -1 0}	1.0
c = 7.2	{-2 0 1}	1.3
$\beta = 116^\circ$	{0 1 0}	0.8
	{0 -1 0}	0.4

Using *SHAPE*

The nuts & bolts of using SHAPE are summarized on the first two pages. The blocks entitled "Getting Started" and "Entering Crystallographic Data" outline the procedures for starting the software and providing the crystal symmetry, form indices, and central distances needed to draw a crystal. The block entitled "Modifying Crystals" describes the options available for "playing with a crystal." This information should be available for reference while in performing the exercises.

Major Disadvantage:

A computer laboratory with a bank relatively fast personal computers is recommended to fully implement the exercises.

MILLER INDICES AND SYMMETRY CONTENT: A DEMONSTRATION USING *SHAPE*, A COMPUTER PROGRAM FOR DRAWING CRYSTALS

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The purpose of this exercise is to use *SHAPE*: A COMPUTER PROGRAM FOR DRAWING CRYSTALS to help you visualize the relationship between the morphology of crystals, Miller indices, axial ratios, crystal faces, open and closed forms to the symmetry content of the crystal.

Instructions on how to create and modify crystal drawings, and how to customize the display, are included at the end of this exercise; that part of the handout is referred to as the "general instruction" handout. Use it as a reference for the specifics of how to use *SHAPE* for this lab. These instructions are written for older (MS-DOS) versions of *SHAPE*. The menu structure in Windows versions is similar. If you can't figure out how to enter some command, ask the instructor for help.

In this exercise, you will generate various crystal drawings, copy them from the screen (using colored pencils), and answer questions about intercepts, Miller indices, symmetry, etc., illustrated by each example. The questions you must answer are printed in bold face. Hand in your drawings, and the answers to the questions, at the end of the lab period, keyed to the filename assigned to each drawing below.

A. TETRAGONAL ($a:c = 1:2$) {111}: First, we will look at how faces with different Miller indices appear in the same crystal class (remember, the crystal class embodies both the coordinate axes and the symmetry content). We will begin with a simple tetragonal crystal. To set this up, go to the general instruction handout, and follow the instructions for creating a new drawing:

1. When prompted for a title, give it any title you want.
2. We will use crystal class $4/m2/m2/m$ for our first few illustrations. Does *SHAPE* accept this, or does it accept a shorthand form? Check the table in the general instruction handout, or in your text, for any necessary equivalencies.
3. Because you entered a crystal class from the tetragonal group ($a_1 = a_2 \neq c$) in the previous step, *SHAPE* knows that it needs only two more numbers; a (because $a_1 = a_2$), and c (which is normally not equal to a). When prompted for the $a:c$ axial ratio, enter 1 2 (for 1:2; be sure to leave a space in between). The unit cell length along the z -direction will be twice that along x & y ; that is, $a:c = 1:2$.
4. You want to generate {111}. Enter the appropriate numerical values of the Miller index now; finish by entering 1 for the central distance.
5. Continue following the general instructions to finish the calculations and put the display on the screen.
6. If everything has gone well, a tetragonal dipyrmaid will now appear on the screen.
7. To see how the axial intercepts for {111} look in $4/m2/m2/m$, $a:c = 1:2$, follow the instructions on the general handout for displaying the axes.
8. If you would like to see what the "hidden" faces at the back of the crystal look like, instruct *SHAPE* to show the back edges.
9. Recalculate and redisplay.

10. The $\{111\}$ tetragonal dipyrmaid should reappear, with axes shown, scaled so that each face intersects each axis at unit length. (IMPORTANT NOTE: The relative lengths of the axes on the screen are proportional to the axial ratio. The unit length $[c]$ in the z -direction is in the present case larger than the unit lengths in the x - or y -directions $[a_1]$ & $[a_2]$, respectively.) On a piece of paper, carefully draw this display. What are the intercepts of the (111) face (top right front) on each of the three axes? How are these intercepts related to the Miller index for the face?
11. Save this file as filename = tetra111.

B. TETRAGONAL ($a:c = 1:2$) $\{112\}$: Next, let's look at what $\{112\}$ looks like, in the same crystal class and with the same axial ratios as in part A. Assuming that $\{112\}$ intersects the x and y axes at one unit length, where does it intersect the z axis? How does this change alter the shape of the resulting crystal?

1. To generate $\{112\}$ with the same symmetry and axial ratios, follow the general instructions for modifying an existing drawing. If we just want to change the Miller index of the form we're trying to visualize (in other words, if we want to see a different form), we need only change the Miller index. Do so as in the general instructions for revising the main crystal.
2. If everything has gone well, an octahedron (actually, an equidimensional tetragonal dipyrmaid) will now appear on the screen. On a piece of paper, carefully draw this display. What are the intercepts of the (112) face (top right front) on each of the three axes? How are these intercepts related to the Miller index for the face?
3. Save this file as filename = tetra112.

C.1. TETRAGONAL, PSEUDOISOMETRIC ($a:c = 1:1$) $\{111\}$: Now, let's see what the same forms $\{111\}$ look like, in the *same* crystal class (i.e., with the same symmetry), but with *different* axial ratios than in parts A & B. Last time, we used $a:c = 1:2$. This time, the unit cell length along the z -direction will be the same as that along x & y ; that is, $a:c = 1:1$. We set the axial lengths to be equal in our example for easy visualization only.

1. Make a new crystal from scratch as in part A of this handout (tetragonal $4/m2/m2/m$), repeating all numbered steps as in part I of the general instructions handout, except that, for the $a:c$ axial ratio, enter 1 (space) 1 (for 1:1). (OR, read existing file tetra111, which you created earlier, and revise the cell parameters.)
2. Observe the axial intercepts. (IMPORTANT NOTE: The relative lengths of the axes on the screen are proportional to the axial ratio. The unit length $[c]$ in the z -direction is now equal to the unit lengths in the x - or y -directions $[a_1]$ & $[a_2]$, respectively.) On a piece of paper, carefully draw this display. What are the intercepts of the (111) face (top right front) on each of the three axes? How are these intercepts related to the Miller index for the face?
3. Save the file as filename = psiso111.

Note; we have identified the symmetry content, and established the relative lengths of the coordinate axes. You may note that we have entered $a_1 = a_2 = c$; usually in the tetragonal crystal class, c does not equal a . Thus, we have set up a situation in which the axial lengths are actually all the same (normally a characteristic of the isometric crystal system), but the symmetry content is lower than that for the isometric crystal system; the symmetry content we have set up is tetragonal ($4/m2/m2/m$). Our example is thus *tetragonal (pseudo-isometric)*. Special cases like this, with special values for some axial length (e.g., length equal to other axes when it is normally not) and/or interaxial angle (e.g., a perpendicular interaxial angle that is normally not, such as β in the monoclinic system), although not common, do exist among minerals. Again, we have set ours

up this way only for ease of visualization.

4. For part C.II. only, we will need to rescale the axes. To do this from the display, see the appropriate part of the general instruction sheet. Try entering 0.67 as the multiplier; the actual value that works for your computer may depend on the graphics card, monitor, &c.

C. II. TETRAGONAL, PSEUDOISOMETRIC ($a:c = 1:1$) {112}:

1. Maintain the symmetry and axial ratios from part C.I.
2. Change the form from {111} to {112}.
3. **On a piece of paper, carefully draw this display. What are the intercepts of the (112) face (top right front) on each of the three axes? How are these intercepts related to the Miller index for the face?**
4. Save the file as filename = psiso112.
5. **Of the four crystal drawings you just created, which two look identical? Why? Can the same crystal shape result from different axial ratios in the same crystal class? What conditions must be satisfied for this to occur?** (Use the "read crystal" option (B on MAIN MENU) to retrieve and re-examine your earlier drawings).
6. For part D, we must rescale the axes back to 1.0. See the paragraph on "rescaling crystal axes" in the general instruction handout, entering 1.0 as the multiplier in menu [N.6], scale option (2).

D. ISOMETRIC: Next, we will investigate how the symmetry content of the crystal class influences the number of faces in a form. We will continue to examine forms {111} and {112}, but this time we will do so in the (true, not pseudo-) isometric crystal class $4/m\bar{3}2/m$. **(Does this crystal class have a shorthand form? What is it?)**

1. ISOMETRIC {111}: Make a new crystal, or revise the existing one; enter the appropriate Hermann-Mauguin symbol for $4/m\bar{3}2/m$; generate {111}.
2. **{111} should appear, with axes shown, scaled so that each face intersects each axis at unit length. What are the intercepts of the (111) face (top right front) on each of the three axes? How are these intercepts related to the Miller index for the face?**
3. Save the present example as filename = iso111.
4. **How does this crystal compare with the one you generated in step C.I (filename = psiso111) and in part B (filename = tetra112)?** (Use the "read crystal" option (B on MAIN MENU) to retrieve and re-examine your earlier drawings).
5. Generate {112}. Examine.
6. **{112} should appear, with axes shown, scaled so that each face intersects each axis at unit length. What are the intercepts of the (112) face (topmost right front) on each of the three axes? How are these intercepts related to the Miller index for the face?**
7. Save as filename = iso112.
8. **Why does form {112} contain a different number of faces in $4/m\bar{3}2/m$ (filename = iso112) than in $4/m2/m2/m$ (which you generated in part C.II; filename = psiso112)?** (Hint: See Tables 2.8 [p. 66] & 2.4 [p. 39] in Klein & Hurlbut.)

E. MONOCLINIC: In the previous parts of this lab, we generated several crystal drawings in the tetragonal and isometric crystal classes, with form {hkl}. In the classes of such high symmetry, invoking the high symmetry generated as many as eight or more faces in a single form (24 in the case of isometric {112}). Now, we will examine forms in crystal classes of lower symmetry (remember, the crystal class embodies both the coordinate axes and the symmetry content).

We began with simple tetragonal and isometric crystals. Review files psiso112 and iso112. Note how the different symmetry content of the two crystal classes generates different

numbers of faces from the same forms. **How many faces are in form {112} in the tetragonal crystal class 4/m2/m2/m? How many faces are in form {112} in the isometric crystal class 4/m $\bar{3}$ 2/m?**

Many minerals (and many other crystalline substances) are monoclinic. Let's look at some of the various forms in monoclinic 2/m. To set this up, refer to the general instructions .

1. Select crystal class 2/m (enter just as written).
2. Because you entered a crystal class from the monoclinic group ($a \neq b \neq c$, $\beta \neq 90^\circ$) in the previous step, SHAPE knows that it needs numbers for all three axes. For the $a:b:c$ axial ratio, enter 0.414 1 0.374 (for 0.414:1:0.374; separating them from one another with a space). When prompted, enter 114 degrees for beta. These are the values for gypsum (see your text). SHAPE will now ask if the values stored are the ones you actually want. Check the list. If everything is OK, just press "ENTER".
3. First, try entering just form {111}, as we did in previous exercises.
4. SHAPE will not let you draw the crystal this way. It will tell you that {111} is not a closed form. **What does this mean?** (Review your text.)
5. You want to generate {010}, {001}, and {111}. Add these forms. For each form, enter the appropriate numerical values of the Miller index now.
6. If everything has gone well, a crystal drawing will now appear on the screen.
7. To see how the axial intercepts look, follow the appropriate instructions on the instructions handout. Also, change the back edge mode as needed.
8. **The crystal drawing should reappear, but now the axes are shown. On a piece of paper, carefully draw this display.**

IMPORTANT NOTE: The relative lengths of the axes on the screen are proportional to the axial ratio. The unit lengths in all three directions are now different from one another, and the y-axis is no longer perpendicular to the other two. Use the arrow keys to tilt and rotate the drawing; observe the faces and axes.

9. Which faces constitute {111}? Use the "form shading" option in menu [N] to shade {111}.
10. Save this file as filename = monoc11.
11. Compare this case (monoc11) with previous examples. In the tetragonal example (tetra111; psiso111) previously, {111} was a dipyrmaid; in the isometric case (iso111), it was an octahedron. Both of these are closed forms. **What does this mean?** (Review your text). In 2/m, {111} is an open form; it does not enclose space fully. We need other faces. In this part of this exercise, we have further examined how the number of faces generated in {111} is different in different crystal classes. We have also seen the difference between closed forms and open forms.

Summary: Several textbooks (likely including the one you're using) state that *the number of faces in (that belong to) a form depends on the symmetry of the crystal class*. (Some texts also discuss how this can also be influenced by the orientation of the face in question with respect to symmetry axes and planes, and how the definitions of general and special forms depend upon the crystal system. We have not actually investigated general forms in most parts of this exercise, but some of the same considerations apply nevertheless.) **Write one paragraph describing how the examples you generated in this lab exemplify what the book is talking about; be specific in referring to specific examples.**

F. STAUROLITE: Now, we will examine the morphological crystallography of staurolite. We will use SHAPE's tilt-rotate function to inspect the symmetry content of several different crystal drawings involving different symmetry content.

1. For this next exercise, you may wish to turn off the crystal axes (toggle is in the [N.6] menu; see the general instruction handout).

2. Most textbooks state that staurolite is monoclinic; $2/m$ (pseudo-orthorhombic). **What is it about the crystallographic parameters shown in the book makes it *pseudo-orthorhombic*?** Is the crystal drawing for staurolite in your text consistent with this? (Your instructor may also provide access to comparable figures from other texts.)
3. (For this question, your instructor may also provide access to Klein & Hurlbut Fig. 13.24, esp. a and b.) **What are the *names* (e.g., prism, pinacoid) of the forms m , b , c , and r present in Klein & Hurlbut Figure 13.24a? (Refer back to your textbook for guidance in naming the forms. Don't use the Klein & Hurlbut chapter 2 text discussion of forms in $2/m$, for reasons we'll talk about later) What are the *Miller indices* of the forms m , b , c , and r present in Klein & Hurlbut Figure 13.24a?**
4. Following the general instructions again, generate a crystal drawing for staurolite using the crystallography stated in the text: symmetry; unit cell lengths a , b & c (given in the text); and the forms you identified in the previous question.

When you enter forms (at least in the DOS version), the Miller index is the first three numbers: the fourth number is the distance from the center of the crystal to the face. Remember, the Miller index tells us about the *ratio of intercepts*; two parallel faces on the same side of the crystal will have the same *ratio* of intercepts, but will be different absolute distances from the center. You have probably noticed that we've been entering "1" for the distance all the time up until now. The first time you generate staurolite, use "1" for all distances. Examine the resulting crystal drawing.

5. Next, we will try to better simulate the drawing in Figure 13.24a. To do so, we will adjust the distances of the forms. We do this by editing the entries we've already made; see the general instruction handout for details. Start with form #1 (the first one on your list); select option 2, modify "Central distance" and enter following distances for the forms: $m = 0.65$; $b = 1.1$; $c = 1.3$; $r = 1.171$. Alternatively, you could start from scratch, using the same axial ratio & symmetry, and entering the same Miller indices, but changing the last of the four digits (the distance). Use the following distances for the forms: $m = 0.65$; $b = 1.1$; $c = 1.3$; $r = 1.171$. The relative overall dimensions of the crystal drawing should now better match Figure 13.24a.
6. Save this file as filename = stauomo.
7. **How does the crystal on the screen now differ from Figure 13.24a? Describe which form(s) and/or face(s) are different, and in what way?** The *size* of each face is not important; by adjusting the central distances, we have made the sizes and shapes of the faces very similar to the drawing; we could make them identical.
8. **What symmetry elements are present in your crystal drawing of staurolite, and how is each symmetry element oriented with respect to the coordinate axes? (You may wish to toggle the crystal axe back on for this) Use the tilt-rotate function (up-down & left-right arrows) to reorient the crystal drawing. (The symmetry elements are, of course, those characteristic of $2/m$; review your text to help you properly orient the axes and the drawing.) Did you save this file as stauomo?**
9. Try adjusting the central differences of the different forms in order to reproduce other staurolite crystal drawings.
10. What symmetry elements are present in Figure 13.24a? What point group are these consistent with (see your text)? It may be easier to see this if we reproduce Figure 13.24a in the text on the computer using SHAPE.
11. Let us guess that the reason the figure in the book differs from the one you just created (using the crystallographic data provided in the book) is because they created the drawing using the wrong crystal class. Let's proceed with the assumption that the drawing in Figure 13.24a exhibits orthorhombic symmetry, in crystal class $2/m2/m2/m$. The easiest way to do this is to just revise the existing crystal; change the crystal class from $2/m$ to $2/m2/m2/m$ (see the table in the general handout, for the "shorthand" form that SHAPE uses). Otherwise, leave everything else the same. What appears on the screen should be essentially identical to Fig. 13.24a.

12. Save this file as filename = stauoor.

13. What symmetry elements are present in Figure 13.24a? What point group are these consistent with (see your text)? What crystal system does 2/m2/m2/m belong to? Is this what the book says about staurolite? So, in what way are the text and the Figure incompatible; what is the "mistake" in Klein & Hurlbut's treatment of staurolite crystallography? (Actually, there are two, but one is more obvious than the other.) If it helps, compare files stauromo & stauoor, using the "read file" option from main menu item B.

Although there is little research in morphological crystallography any more, the example you are working on is one where there is a genuine scientific problem, and it is a problem in which morphological crystallography once played an important role.

Staurolite is a metamorphic mineral, that seems to be able to form under several different sets of conditions. This is known in metamorphic petrology as "the staurolite enigma". To correctly interpret staurolite occurrences the thermodynamic properties of the mineral must be better determined; knowing the chemical energetics (thermodynamics) requires knowing the coordination environment, bonding, etc., of all elements present - in other words, the crystal structure. The earliest X-ray diffraction work on staurolite (in the 1920s) suggested that the mineral is orthorhombic. However, in the 1950s, a student in a mineralogy class at Johns Hopkins University observed that the morphological crystallography of staurolite specimens from Georgia in the teaching collection were inconsistent with orthorhombic symmetry, but were instead consistent with monoclinic. For the last 40 years, researchers have been trying to solve this problem. The most recent research (1993-4) suggests that there are both monoclinic and orthorhombic staurolites, with possibly different properties. Research continues on this petrologically important problem. Careful examination of morphological crystallography provided early major insights into this problem.

For a wonderful historical review of staurolite crystallography (1792-1983), emphasizing morphological crystallography, early X-ray crystallography, and the role of perceptive students in scientific progress, see Donnay, J.D.H., and Donnay, G. (1983), The Staurolite Story, *Tschermaks Mineralogische und Petrographische Mitteilungen*, v. 31, p. 1-15. For a comprehensive discussion of recent progress from X-ray crystallography, see the three-part series of papers by F.C. Hawthorne and his colleagues (1993) in *Canadian Mineralogist*, v. 31, The crystal chemistry of staurolite; part I (p. 551-582), part II (p. 583-595) and part III (p. 597-616).

It is instructive to measure some interfacial angles on real staurolite crystals, and compare them with the data and drawings in the textbooks.

GENERATING CRYSTAL DRAWINGS USING SHAPE: A COMPUTER PROGRAM FOR DRAWING CRYSTALS

This handout provides general instructions for generating crystal drawings using SHAPE: A COMPUTER PROGRAM FOR DRAWING CRYSTALS. Several lab exercises will use SHAPE to help you visualize the relationship between the morphology of crystals, Miller indices, axial ratios, stereographic projections and face poles, and the relationships of crystal faces and forms to the symmetry content of the crystal.

SHAPE is menu-driven. Hit the RETURN (ENTER) key after each command. Computers already have SHAPE loaded and running. Most benches have a copy of the SHAPE manual. The manual is for reference, and may not leave the computer. If you can't figure out how to enter some command, ask the instructor for help.

These instructions are written for older (MS-DOS) versions of SHAPE. The menu structure in Windows versions is similar.

I. HOW TO GENERATE A CRYSTAL DRAWING:

A. Selecting crystal class and cell parameters.

1. Enter a new crystal (option A on MAIN MENU).
2. When prompted, give it any title you want.
3. Select the crystal class. Use Hermann-Mauguin notation (as summarized in, e.g., Blackburn & Dennen Table 2.4). Note that some of the crystal classes can be written in a "shorthand" form; equivalencies shown here are from Table 2.8 in Dana. Where the "shorthand" form exists, it is the one SHAPE uses.

EQUIVALENT LONG AND ABBREVIATED FORMS OF SIX CRYSTAL CLASSES

System	Long Form	Short Form
Orthorhombic	2/m2/m2/m	mmm
Tetragonal	4/m2/m2/m	4/mmm
Hexagonal	$\bar{3}2/m$ 6/m2/m2/m	$\bar{3}/m$ 6/mmm
Isometric	2/m $\bar{3}$ 4/m $\bar{3}2/m$	m3 m3m

4. Next, SHAPE will prompt you for the axial ratio. Where two or more axes must be equal due to the point group symmetry of the crystal class, SHAPE knows which ones must be equal by definition, so it will only prompt you for what is appropriate (SHAPE will not ask for extraneous information). SHAPE will accept either the axial ratios (available in most older mineralogy texts), or the unit-cell dimensions in Angstroms; SHAPE will calculate the ratio from the dimensions in the latter case. Enter each axial length, separating each by a space.
5. If the crystal class of interest is monoclinic or triclinic, SHAPE will prompt you for the interaxial angle(s), as appropriate. Otherwise, SHAPE will set the angles according to the requirements of the point group symmetry of the crystal class.
6. SHAPE will now ask if the values stored are the ones you actually want. Check the list. If everything is OK, just press "ENTER".

B. Entering Miller indices and central distances.

1. SHAPE will next ask for the Miller index of each form you want to generate, and how far from the center of the crystal you want the faces in that form to be (more on this

later). For any arbitrary form $\{hkl\}$ at a distance of one, enter the numbers for h , k , and l as follows:

h (space) k (space) l (space) 1 (for distance) ENTER.

The first three digits are the Miller index, which define the orientation ("slope") of the face relative to the axes; the fourth tells SHAPE how far out from the center of the crystal you want the face with that "slope" drawn. For each of the form(s) you want to generate, enter the appropriate numerical values of the Miller index now.

2. To let SHAPE know that you are done entering the list of forms, enter:
99 (space) 0 (space) 0 (space) 0 ENTER.
3. SHAPE will now ask if the list of forms is correct. Check the list; if OK, press "ENTER".
4. Next, you will be given the chance to revise the forms on the list. The first time around, decline this option by "ENTER"ing.
5. **If everything has gone well, an crystal drawing will now appear on the screen.**
6. To return to the MAIN MENU from the display screen, hit the SPACEBAR once.

II. SAVING AND READING FILES

A. To save a file:

From the MAIN MENU:

1. Select the "save" option (B, Read or save crystal file).
2. Then on menu [B], select option 1 "Write file".
3. Save the file by assigning it an 8 character filename.

B. To read a file already created:

From the MAIN MENU:

1. Select the "read" option (B, Read or save crystal file).
2. Then on menu [B], select option 2 "Read file (new format)".
3. Read the file by entering its 8 character filename.

III. CUSTOMIZING THE DISPLAY

A. To see how the axial intercepts look, do the following:

1. Return to the MAIN MENU by hitting the spacebar once.
2. Select "Display modes and options" (N on the MAIN MENU).
3. When the "Display modes and options" menu appears, select "crystal axes" (option 6).
4. In the [N.6] menu, select the on/off toggle (option 1), and toggle "on". When finished, "ENTER" (to leave [N.6] menu).
5. We should now be in the [N] menu.
6. "ENTER" again (to leave [N] menu).
7. Upon return to MAIN MENU, select "Replot on screen" (D).
7. **The crystal drawing should reappear, but now the axes are shown, their lengths proportional to the axial ratio you specified, and usually scaled so that each face intersects each axis at unit length.**
8. To return to the MAIN MENU from the display screen, hit the SPACEBAR once.

B. Rescaling the axes.

For some purposes, we will need to rescale the axes. To do this from the display:

1. Return to the MAIN MENU by hitting the spacebar once.
2. Select "Display modes and options" (N on the MAIN MENU).
3. When the "Display modes and options" menu appears, select "crystal axes" (option 6).
4. When you get to the [N.6] menu (step 11), select the scale option (2).
5. Enter the new multiplier (1.0 leaves the axes the same size; a $\# > 1$ enlarges them, a $\# < 1$ makes them smaller).

6. When finished, "ENTER" (to leave [N.6] menu). We should now be in the [N] menu.
7. "ENTER" again (to leave [N] menu).
8. Upon return to MAIN MENU, select "Replot on screen" (D).
9. **The crystal drawing should reappear, but now the axes are shown, their lengths proportional to the axial ratio you specified, and now rescaled as you instructed.**
10. To return to the MAIN MENU from the display screen, hit the SPACEBAR once.

C. To see "hidden" faces:

As we have set it up so far, SHAPE draws the outlines of crystal faces for the front faces only. If you would like to see what the "hidden" faces at the back of the crystal look like, we must instruct SHAPE to show us the back edges. To do so, we change the back edge mode as follows:

From the MAIN MENU,

1. Select "Display modes and options" (N on the MAIN MENU).
2. When the [N] "Display modes and options" menu appears, select "back edge mode" (option 2).
3. When in menu [N.2], select option 1 (dashed) to draw the back edges as dashed lines (most people will find this easier than trying to sort out front from back if both are plotted as solid lines, especially on monochrome monitors). When finished, press "ENTER" (to leave [N.2] menu).
4. "ENTER" again (to leave [N] menu).
5. Upon return to MAIN MENU, select "Replot on screen" (D).
6. **The crystal drawing should reappear, with back edges shown as you instructed.**
7. Return to the MAIN MENU by hitting the spacebar once.

D. Rotating the crystal.

The orientation of the crystal drawing on the screen can be modified by using the arrow keys on the keyboard.

E. Other customizing options exist, including changing the colors and solid/dashed drawing of front-edge lines, back-edge lines, and axes. These are described in the manual.

IV & V: MODIFYING EXISTING CRYSTAL DRAWINGS, AND MAKING MAJOR CHANGES FROM EXISTING CRYSTAL DRAWINGS

These instructions show you how to make changes on a crystal that's already been drawn.

1. To return to the MAIN MENU from the display screen, hit the SPACEBAR once.
2. From the MAIN MENU, select (A) Enter or revise main crystal.
3. Then select (0) Revise main crystal. (Starting over would basically take you back to the beginning, as in part I.)
4. The "Revise original crystal" screen should now display choices including (1) Revise title, crystal system, cell parameters, (2) Revise forms, and (3) Remove symmetry - convert faces to forms. This is the jumping-off point for all the following modifications.

IV. MODIFYING EXISTING CRYSTAL DRAWINGS: ADDING, DELETING, AND MODIFYING INDIVIDUAL FORMS

To add new form(s) or delete or modify existing ones, proceed as follows:

From the "Revise original crystal" screen:

1. Select (2) Revise forms, by entering 2 at the prompt. SHAPE will list the form(s) you've already selected.
2. Press ENTER to continue. A list of revision options will appear below the list of previously selected forms. This is called the "Revise Forms" list.

A. To add new form(s) or delete existing ones, proceed as follows:

Adding new form(s).

New forms can be added to your crystal using the following procedure.

1. From the "Revise Forms" list, select 4) Add forms, by entering 4 at the "Choice?" prompt.
2. When prompted, enter indices (hkl) and central distance for each form you want to add, as in part I.
3. End the list of forms with 99 0 0 0 (as in part I).

Removing form(s).

To delete a form,

1. From the "Revise Forms" list, select 3) Delete forms, by entering 3 at the "Choice?" prompt.
2. Select which form number(s) you want to delete from the list; enter the number of the first and the last you want to delete (separated by a space; if you only want to delete one, enter its number twice).
3. Enter 0 0 (separated by a space).

B. Changing a form to a different form.

To stop looking at one form and start looking at a different one, with everything else being held constant, you can either simply delete the old one and add the new one, or you can change from one to the other as follows:

1. From the "Revise Forms" list, select 1) "Revise individual form", by entering 1 at the "Choice?" prompt.
2. Select option 1 "Indices".
3. Enter the appropriate integer values for $\{hkl\}$ (here, you need only enter the three integers for the Miller index; keep the same central distance).

C. Adjusting the size of faces.

To change the size of the crystal faces in a form relative to the size of the faces in other forms, change the central distance. The central distance is the shortest distance from the origin (where all the axes intersect) to the crystal face (the shortest distance will be along a line perpendicular to the face). Decreasing the central distance (making the face closer to the origin) makes that face larger relative to the other faces; increasing the central distance (moving the face farther from the origin) makes that face smaller relative to the other faces.

To change the size of the faces in a form:

1. Determine which form from the list of forms you want to change. SHAPE keeps track of them by their place in the list; the first one (listed as form 1) is 1, the next is 2, etc.
2. From the "Revise Forms" list, select 1) , by entering 1 at the "Choice?" prompt.
3. Enter the "Number of form to revise?" (Item number; 1, 2, 3....)
4. From the next menu, modify item 2) Central distance, by entering 2 after the "Number to modify?" prompt.
5. Enter the new multiplier (1.0 leaves the axes the same size; a $\# > 1$ enlarges them, a $\# < 1$ makes them smaller).

V. MAKING MAJOR CHANGES FROM EXISTING CRYSTAL DRAWINGS

Sometimes we might want to compare the crystal we're working on (with its symmetry, axial ratio, forms, etc.) with another crystal that differs in only one way from the one we've already made. We could make the new crystal completely from scratch (start completely over, making a new drawing, as in part I of these instructions). However, if we only want a few things to be different, it's usually easier (certainly shorter) to make the new crystal by just changing the thing(s) we want to change, using the one we've already made as our starting point. The following instructions show how to do this.

A. Changing the symmetry.

1. Select (1) Revise crystal system, by entering 1 at the prompt.
2. From the "Revise title, crystal class, cell parameters" menu, select 2) crystal class.
3. On the "Now select crystal class" screen, select the new crystal class by entering the appropriate code for the class you want from the list.

B. Changing the axial ratio.

To see what the same form(s) look(s) like, in the *same* crystal class (i.e., with the same symmetry), but with *different* axial ratios:

1. Select (1) Revise crystal system, by entering 1 at the prompt.
2. From the "Revise title, crystal class, cell parameters" menu, select 3), 4) and/or 5)
CONTINUE.

IV & V: To see the modified drawing:

1. Check the list of forms and their central distances; if OK, proceed to the next step.
2. From the "Revise Forms" list, select nothing; do this by just hitting ENTER after the "Choice?" prompt. Making no "Choice?" takes you back to the previous ("Revise original crystal") menu.
3. From the "Revise original crystal" list, again select nothing; do this by just hitting ENTER after the prompt.
SHAPE will then prompt "Recalculate and redisplay (Y/N)?"
4. Enter y (for yes) and the revised crystal will appear.

VI. INFORMATION RETRIEVAL USING SHAPE

Once you have created or retrieved a crystal drawing, you can instruct SHAPE to highlight an individual face, or all faces in a form.

A. To highlight a face or form:

1. Return to the MAIN MENU by hitting the spacebar once.
2. Select "Display modes and options" (N on the MAIN MENU).
3. When the [N] "Display modes and options" menu appears, select "fills and shading" (option 4).
4. In the [N.4] menu, select the "Face form or fill" toggle (option 1), and toggle "on".
5. From the [N.4.1] menu, select 2) Individual fills; answer Y to add new one(s).

6a. Highlighting a face.

Any face can be identified by selecting 0 at the appropriate place in [N.4.1], and entering the desired Miller index. Select a color, and proceed to redisplay.

6b. Highlighting a form.

All faces in a chosen form can be identified by selecting 1 at the appropriate place in [N.4.1], and entering the desired Miller index. Select a color, and proceed to redisplay.

7. When finished, "ENTER" (to leave [N.4] menu).

We should now be in the [N] menu.

8. "ENTER" again (to leave [N] menu).

9. Upon return to MAIN MENU, select "Replot on screen" (D).

10. The crystal drawing should reappear, but now the face or form you selected is shown in the color you selected.

11. To return to the MAIN MENU from the display screen, hit the SPACEBAR once.

B. Interfacial angles.

The interfacial angle between any two faces on your crystal can be calculated (if indices of the two faces are known) by using the INTERFACIAL ANGLE option (select G from the MAIN MENU).

I would like to thank Prof. Ken Brock (Indiana University Northwest; Gary, IN) for inspiring me to assemble these instructions in this format.

CRYSTAL MEASUREMENT AND AXIAL RATIO LABORATORY

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Goals of the Exercise

This exercise is designed to help you understand relationships among external morphology of crystals (their shape and faces), internal structure (unit cell shape, edge measurements, and volume), Hermann-Mauguin notation for the 32 crystal classes, and Miller Indices of forms and faces. When you look up the information on any mineral in a standard reference or text book such as Dana's *Manual of Mineralogy* (Klein and Hurlbut, 1993) or *Introduction to the Rock Forming Minerals* (Deer, Howie, and Zussman, 1966) you will note that the following crystallographic information is given: crystal class in Hermann-Mauguin notation, axial ratios (relative unit cell lengths), absolute unit cell lengths (in Ångstrom units), and common crystal forms present in terms of Miller Indices. Some references may also give Φ (Phi) and ρ (Rho) values for each form. These values have been determined by measurement of the external form of the crystal and can be used to plot the forms or faces on a Wulff stereographic projection. This exercise should help you to understand and use this standard mineralogical information.

Before proceeding with the exercise you should have an understanding of the symmetry elements present in the 32 crystal classes and how they are represented by Hermann-Mauguin notation. You should also understand the differences between the axial ratio and absolute cell lengths of a mineral, the meaning and use of Miller Indices, and how mineral faces and forms are plotted on a Wulff stereographic projection. These subjects are covered with examples in most mineralogy textbooks.

How Crystals are Measured

Each crystal face can be identified by two angular measurements, Φ (Phi) and ρ (Rho). The Rho angle is the angle measured along a great circle from the **c**-crystallographic axis to the **face pole** (a line perpendicular to the face). The Phi angle is the angle measured in the plane of the equator of the crystal from the **+ b** axis to the great circle in which the face pole is located. These measurements are similar to the latitude and longitude of any geographic location on earth. Longitude is measured from the Greenwich meridian (a great circle passing through the north and south poles) in the plane of the equator to the great circle on which the geographic location is located. Latitude is measured along a great circle from the equator to the geographic location. Great circles are circles that pass through both the north and south pole (longitude in geographical terms); small circles are planes parallel to the equator (latitude in geographical terms).

Measurements are made by an instrument called a **goniometer**. These can range from very sophisticated two-circle models with microscope and telescope to a very simple one made with a protractor and ruler. All goniometers are designed to measure the interfacial angles between perpendiculars to faces (face poles). Examples of goniometers and how to use them are found in mineralogy textbooks such as *Manual of Mineralogy*, (Klein and Hurlbut, 1993).

Measurements on a goniometer are usually made in **zones**. All faces are said to be in a zone if they all lie parallel to one crystallographic direction, e.g. all faces parallel to a **c**-crystallographic axis are in the same zone. The sum of all angles measured between face poles in a zone should be 360° . If the total is not 360° a mistake has been made -- either a number was read wrong or an angle missed that should be measured.

Faces are grouped together in **forms**. Each face in a form has the same angular relationship to each of the crystallographic axes. The Form symbol chosen is that for the most positive face, e.g. for a cube there are 6 faces (001), (00 $\bar{1}$), (100), ($\bar{1}$ 00), (010), (0 $\bar{1}$ 0) and the form symbol chosen is {100}. Notice that braces are used to indicate forms.

The Wulff Stereographic Projection

Once a crystal has been measured and each face assigned Φ and ρ values, one can then plot the faces on a Wulff stereonet (also known as an equal angle net) to determine the symmetry of the crystal, and thus, to determine the crystal class to which it belongs. The description of the method of plotting faces on a Wulff projection are found in all mineralogy textbooks such as *Manual of Mineralogy* (Klein and Hurlbut, 1993).

Calculating the Axial Ratio

After you have measured a crystal, plotted all the faces on a stereographic projection, determined all the symmetry elements present, and determined the crystal system to which the crystal belongs, you are then ready to calculate the axial ratios. You first must choose a face that cuts all three crystallographic axes and arbitrarily give it the Miller Index (111). This is called a **parametral plane**. When more than one form cuts all three crystallographic axes it is customary to take the form with the larger faces as the parametral plane, however, either one could be chosen.

It is not necessary to calculate an axial ratio for an isometric crystal because all three crystallographic axes are the same length and all angles are 90°. However, it is possible to calculate axial ratios for a crystal in any of the other crystal systems. Axial ratio's for the tetragonal and hexagonal crystal systems are written **a:c** where **a = 1** (by convention) and the axial ratio's for the orthorhombic, monoclinic and triclinic crystal systems are written as **a:b:c** where **b = 1** (also by convention). This exercise deals only with crystals in the tetragonal and orthorhombic crystal systems to simplify the calculations needed. Calculations for other crystal systems are simplified by a matrix algebra approach (see Gibbs, this volume). The equations for **a** and **c** are as follows:

$$a = h (\cot \Phi) / k$$

$$c = l (\tan \rho) (\cos \Phi) / k$$

where **h**, **k**, and **l** are from the Miller Index for the face (**hkl**) and are all one if the face is (111).

Calculation of Miller Indices

Once an axial ratio is determined for a crystal by the equations above, it is possible to calculate the Miller Index of each face or form on the crystal using the same equations in a slightly different form as shown below:

$$k / h = (\cot \Phi) / a$$

$$k / l = (\tan \rho) (\cos \Phi) / c$$

Keep in mind that once an axial ratio is determined for a crystal, the same value for **a** and **c** should be used to calculate the Miller Index of each face. There are several exceptions: (1) Any face that cuts one axis and is parallel to two other axes can be indexed by inspection, e.g. (001), (010), or (00 $\bar{1}$); and (2) it is not possible to calculate the Miller Index for any face parallel to the **b**-axis as the angle $\Phi = 90^\circ$ and thus the cosine and cotangent values in the above formulas would be 0. A practical solution to the problem is to exchange the **a** and **b** values in the axial ratio, divide **a**, **b**, and **c** with the old **a** value, and use the new **a** and **c** values in the above equation for that face (**a:b:c** is **a:1:c = 1/a : 1/a : c/a**). (See the worked example.)

A Checklist for Crystal Measurement

- 1) Make a sketch of the mineral and label each face with a small letter such as a, b, c, etc. to identify the face.
 - 2) Measure all interfacial angles by zones and list the angles for each zone.
 - 3) Chose an orientation for the mineral and make an angle table of Φ and ρ values.
 - 4) Plot each face on a Wulff projection using the Φ and ρ values for each face.
 - 5) Determine the symmetry elements that are present from the arrangement of the faces, mark the symmetry on the net, from this determine the crystal class, and label your diagram with the Hermann-Mauguin notation for that class.
 - 6) Choose one face which cuts all three axes as the parametral plane and arbitrarily give it the Miller Index (1 1 1).
 - 7) Calculate the axial ratio.
 - 8) Group the faces into forms and make a Table of Forms.
 - 9) Calculate the Miller Index for each of the remaining forms.
-

References

- Klein, C. and Hurlbut, C.S., Jr., (1993) *Manual of Mineralogy*, 21st Edition: New York, John Wiley and Sons, 681p.
- Deer, W.A., Howie, R.A., and Zussman, J. (1966) *An Introduction to the Rock-Forming Minerals*: New York, John Wiley and Sons, 528p.

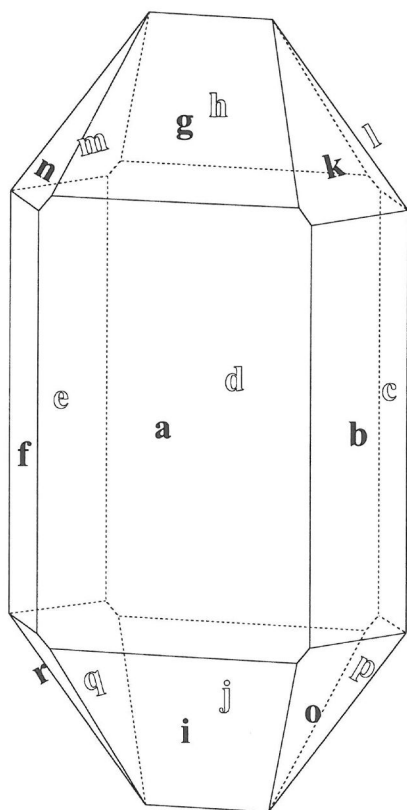
Notes for the Instructor

The example and four crystal measurement problems have been drawn using the computer program SHAPE (see both Brock and Velbel, this volume). Both a single drawing and stereo pair are given for each problem. The stereo pair drawings can be used with the normal stereoscope used to read air photographs. The interfacial angles were calculated by the SHAPE program. If you have access to SHAPE you can design other crystal problems or have students generate the crystal drawing on the computer and then make the calculations ask for in this exercise.

Some geology departments still have access to wooden crystal models (Krantz models). Students can make a simple goniometer with a plastic protractor and ruler and then measure the interfacial angles on the wooden models. They then can make the drawings and angle tables themselves rather than using the computer program.

Example of a Crystal Measurement and Calculation

The crystal drawing and interfacial table for a crystal are shown below:



Interfacial Angles

$$a \wedge b = 58.47^\circ$$

$$b \wedge c = 63.06^\circ$$

$$c \wedge d = 58.47^\circ$$

$$d \wedge e = 58.47^\circ$$

$$e \wedge f = 63.06^\circ$$

$$f \wedge a = 58.47^\circ$$

$$a \wedge g = 31.89^\circ$$

$$g \wedge h = 116.23^\circ$$

$$h \wedge d = 31.89^\circ$$

$$d \wedge i = 31.89^\circ$$

$$i \wedge j = 116.23^\circ$$

$$j \wedge a = 31.89^\circ$$

$$b \wedge k = 33.05^\circ$$

$$k \wedge m = 113.90^\circ$$

$$m \wedge e = 33.05^\circ$$

$$e \wedge q = 33.05^\circ$$

$$q \wedge o = 113.90^\circ$$

$$o \wedge b = 33.05^\circ$$

$$f \wedge n = 33.05^\circ$$

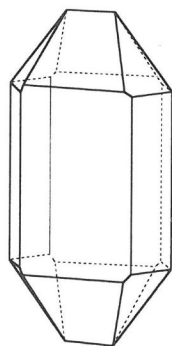
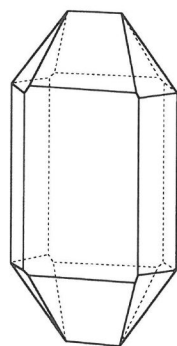
$$n \wedge l = 113.90^\circ$$

$$l \wedge c = 33.05^\circ$$

$$c \wedge p = 33.05^\circ$$

$$p \wedge r = 113.90^\circ$$

$$r \wedge f = 33.05^\circ$$

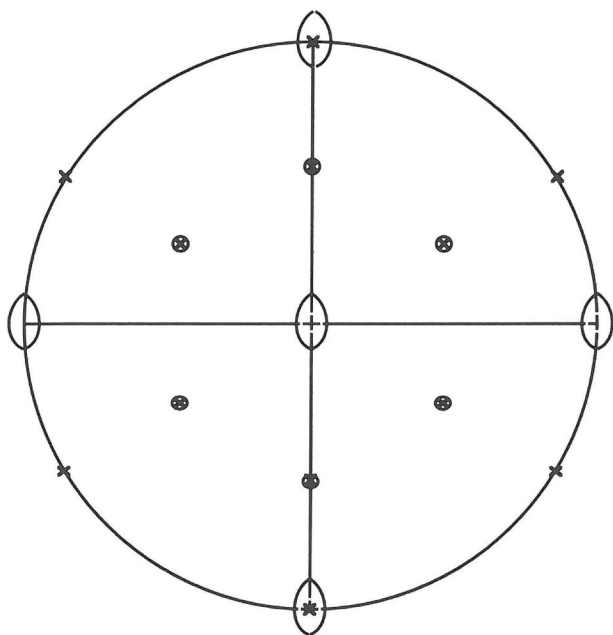


Orient the crystal so that the **a**, **b**, and **c** crystallographic axes are parallel to symmetry axes and calculate the Φ and ρ values for each face.

Angle Table:

<u>face</u>	<u>Φ</u>	<u>ρ</u>
a	90°	90°
b	31.53°	90°
c	-31.53°	90°
d	-90°	90°
e	-148.47°	90°
f	148.47°	90°
g	90°	58.12°
h	-90°	58.12°
i	90°	-58.12°
j	-90°	-58.12°
k	31.53°	56.95°
l	-31.53°	56.95°
m	-148.47°	56.95°
n	148.47°	56.95°
o	31.53°	-56.95°
p	-31.53°	-56.95°
q	-148.47°	-56.95°
r	148.47°	-56.95°

Wulff Projection of all Faces and Symmetry



Hermann-Mauguin symbol for the symmetry shown is **2/m 2/m 2/m**.

Table of Forms

<u>Form</u>	<u>Miller Index</u>	<u>Φ</u>	<u>ρ</u>
a,d	{100}	90°	90°
b,c,e,f	{110}	31.53°	90°
k,l,m,n,o,p,q,r	{111}	31.53°	56.95°
g,h,i,j	{201}	90°	58.12°

Calculation of the Axial Ratio

Use the Parametral plane (111) which you have arbitrarily chosen because it cuts all three crystallographic axes.

$$a = h (\cot \Phi) / k = 1 (\cot 31.53^\circ) / 1 = 1.63$$

$$c = l (\tan \rho) (\cos \Phi) / k = 1 (1.537) (0.852) / 1 = 1.31$$

$$a:b:c = 1.63:1:1.31$$

Calculation of the Miller Index for Each Form

{111} This is the parametral form and is arbitrarily chosen as (111).

{100} Each face in this form cuts only one axis and is parallel to the other two axes. The index is chosen by inspection.

{110} This form is parallel to the **c**-axis and cuts the **a**- and **b**-axes, thus, only one equation is needed.

$$k / h = (\cot \Phi) / a = 1.63 / 1.63 = 1 / 1; \text{ thus the Miller Index is (110)}$$

{201} Whenever a face has a Φ value of 90° the above equations will not work because the cotangent and cosine functions are 0 for 90°. A simple trick can be used to get rid of this $\Phi = 90^\circ$ problem by rotating the crystal 90° and making $\Phi = 0^\circ$.

$$a:b:c = 1.63:1:1.31$$

exchange the **a** and **b** axes thus **b:a:c** = 1:1.63:1.31

$$\text{Divide through by 1.63} \quad (1/1.63):(1.63/1.63):(1.31/1.63) = 0.613:1:0.804$$

Use the axial ratio **a:b:c** = **0.613:1:0.804** together with $\Phi = 0^\circ$ and the ρ value for the form to calculate the Miller Index.

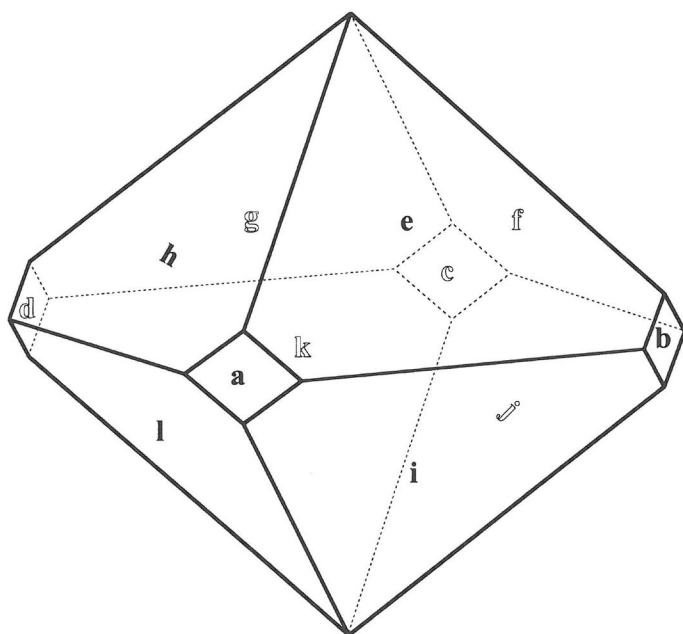
The faces of the form are all parallel to the new **a**-axis so the **h** value in the new Miller Index will be 0 and only the following equation need be used:

$$k / l = (\tan \rho)(\cos \Phi) / c = (\tan 58.12^\circ)(\cos 0^\circ) / 0.804 = (1.608)(1) / 0.804 = 2/1$$

The Miller Index would be (021), however, if the crystal is rotated back to its original position according to the original axial ratio (**a** exchanged for **b**), then the Miller Index is (201).

CRYSTAL MEASUREMENT EXERCISES

Crystal #1



Interfacial Angles

$$a \wedge b = 90^\circ$$

$$b \wedge c = 90^\circ$$

$$c \wedge d = 90^\circ$$

$$d \wedge a = 90^\circ$$

$$e \wedge i = 83.59^\circ$$

$$i \wedge k = 96.41^\circ$$

$$k \wedge g = 83.59^\circ$$

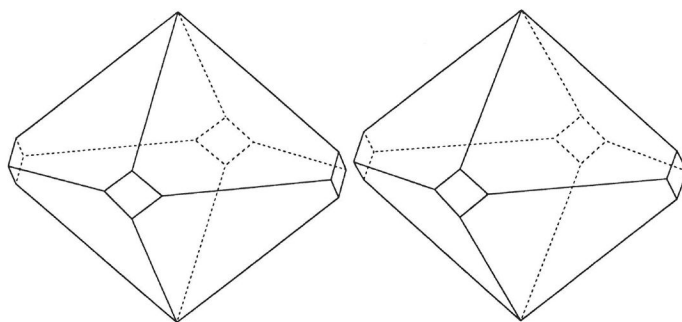
$$g \wedge e = 96.41^\circ$$

$$h \wedge l = 83.59^\circ$$

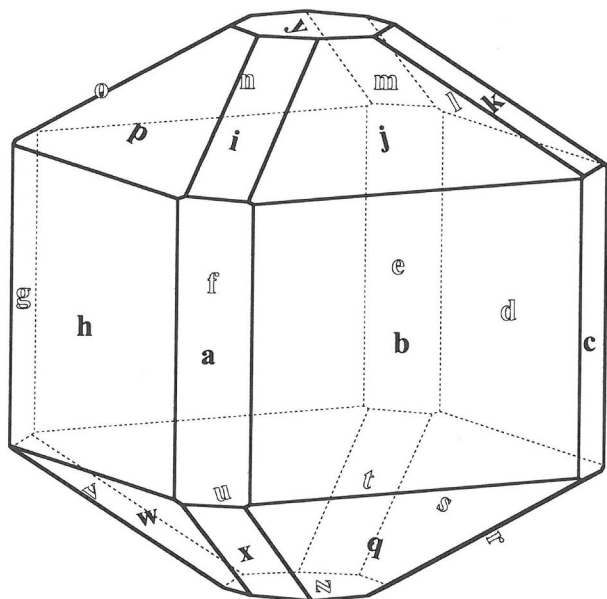
$$l \wedge j = 96.41^\circ$$

$$j \wedge f = 83.59^\circ$$

$$f \wedge h = 96.41^\circ$$



Crystal #2



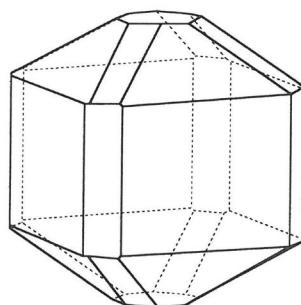
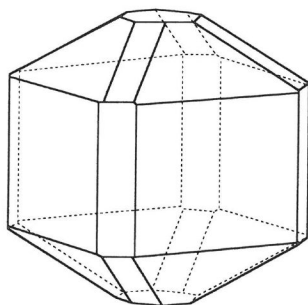
Interfacial Angles

$a \wedge b = 45^\circ$	$y \wedge k = 29.98^\circ$
$b \wedge c = 45^\circ$	$k \wedge c = 60.02^\circ$
$c \wedge d = 45^\circ$	$c \wedge r = 60.02^\circ$
$d \wedge e = 45^\circ$	$r \wedge z = 29.98^\circ$
$e \wedge f = 45^\circ$	$z \wedge v = 29.98^\circ$
$f \wedge g = 45^\circ$	$v \wedge g = 60.02^\circ$
$g \wedge h = 45^\circ$	$g \wedge o = 60.02^\circ$
$h \wedge a = 45^\circ$	$o \wedge y = 29.98^\circ$

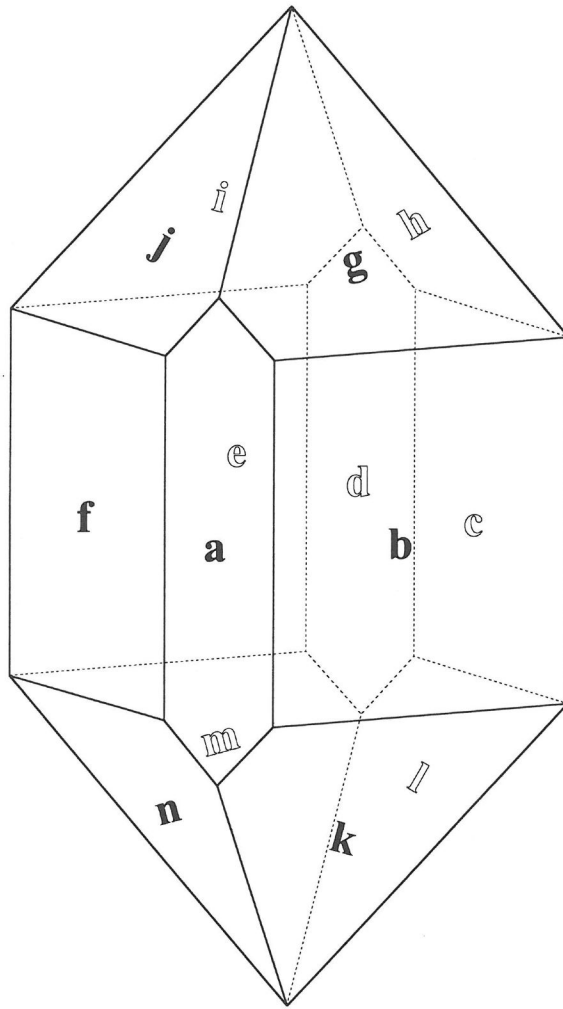
$y \wedge j = 39.21^\circ$
$j \wedge b = 50.79^\circ$
$b \wedge q = 50.79^\circ$
$q \wedge z = 39.21^\circ$
$z \wedge u = 39.21^\circ$
$u \wedge f = 50.79^\circ$
$f \wedge n = 50.79^\circ$
$n \wedge y = 39.21^\circ$

$y \wedge p = 39.21^\circ$
$p \wedge h = 50.79^\circ$
$h \wedge w = 50.79^\circ$
$w \wedge z = 39.21^\circ$
$z \wedge s = 39.21^\circ$
$s \wedge d = 50.79^\circ$
$d \wedge l = 50.79^\circ$
$l \wedge y = 39.21^\circ$

$y \wedge i = 29.98^\circ$
$i \wedge a = 60.02^\circ$
$a \wedge x = 60.02^\circ$
$x \wedge z = 29.98^\circ$
$z \wedge t = 29.98^\circ$
$t \wedge e = 60.02^\circ$
$e \wedge m = 60.02^\circ$
$m \wedge y = 29.98^\circ$



Crystal # 3



Interfacial Angles

$$a \wedge b = 43.47^\circ$$

$$b \wedge c = 93.06^\circ$$

$$c \wedge d = 43.47^\circ$$

$$d \wedge e = 43.47^\circ$$

$$e \wedge f = 93.06^\circ$$

$$f \wedge g = 43.47^\circ$$

$$g \wedge b = 32.02^\circ$$

$$b \wedge k = 32.02^\circ$$

$$k \wedge m = 115.95^\circ$$

$$m \wedge e = 32.02^\circ$$

$$e \wedge i = 32.02^\circ$$

$$i \wedge g = 115.95^\circ$$

$$j \wedge f = 32.02^\circ$$

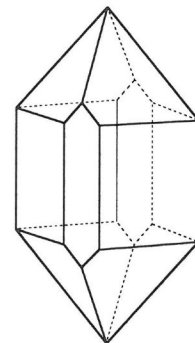
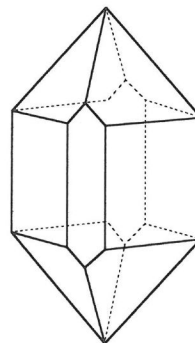
$$f \wedge n = 32.02^\circ$$

$$n \wedge l = 115.95^\circ$$

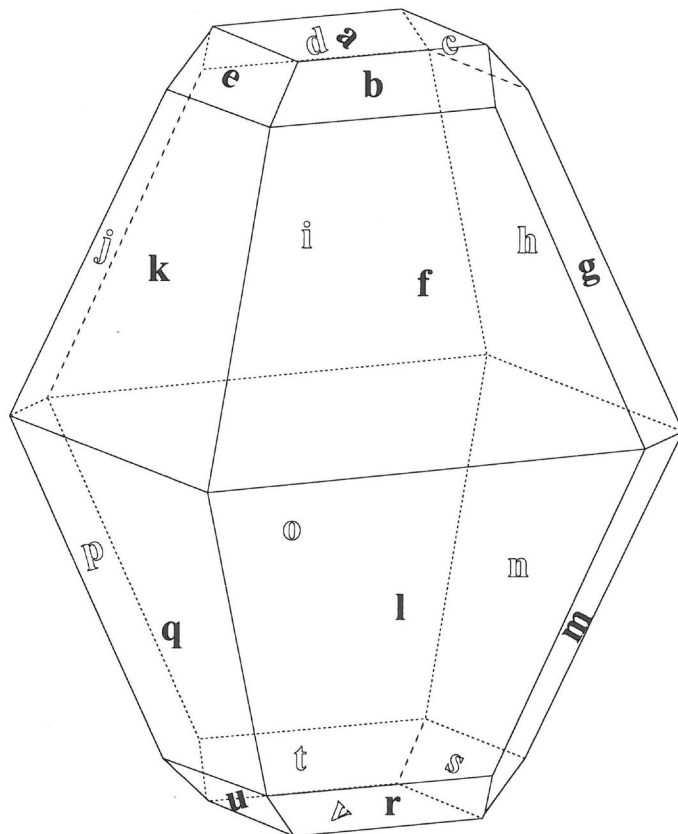
$$l \wedge c = 32.02^\circ$$

$$c \wedge h = 32.02^\circ$$

$$h \wedge j = 115.95^\circ$$



Crystal # 4



Interfacial Angles

$$a \wedge g = 64.54^\circ$$

$$g \wedge m = 50.93^\circ$$

$$m \wedge v = 64.54^\circ$$

$$v \wedge p = 64.54^\circ$$

$$p \wedge j = 50.93^\circ$$

$$j \wedge a = 64.54^\circ$$

$$a \wedge b = 42.85^\circ$$

$$b \wedge f = 27.38^\circ$$

$$f \wedge l = 39.53^\circ$$

$$l \wedge r = 27.38^\circ$$

$$r \wedge v = 42.85^\circ$$

$$v \wedge t = 42.85^\circ$$

$$t \wedge o = 27.38^\circ$$

$$o \wedge i = 39.53^\circ$$

$$i \wedge d = 27.38^\circ$$

$$d \wedge a = 42.85^\circ$$

$$a \wedge e = 42.85^\circ$$

$$e \wedge k = 27.38^\circ$$

$$k \wedge q = 39.53^\circ$$

$$q \wedge u = 27.38^\circ$$

$$u \wedge v = 42.85^\circ$$

$$v \wedge s = 42.85^\circ$$

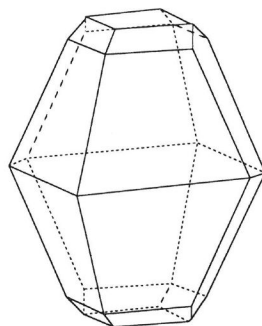
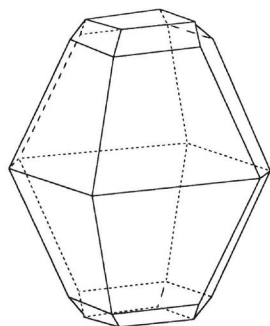
$$s \wedge n = 27.38^\circ$$

$$n \wedge h = 39.53^\circ$$

$$h \wedge c = 27.38^\circ$$

$$c \wedge a = 42.85^\circ$$

$$h/n \text{ edge} \wedge f/l \text{ edge} = 82.02^\circ$$



THE USE OF NATURAL CRYSTALS IN THE STUDY OF CRYSTALLOGRAPHY

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INTRODUCTION

I use single, euhedral, natural crystals of minerals extensively when teaching basic concepts of crystallography. Wooden or paper models, showy museum-quality crystal clusters, colorful pictures in a book, or even computer images simply cannot compete with the beauty, awe-inspiring mystery and educational value of genuine, individual mineral crystals when held in your (or your students'!) hands.

Most Mineralogy courses include lecture material and lab exercises on crystallography. Why not have students work with real crystals as much as possible? From my experience, this can be a lot of fun for everyone and seems to effectively engage the students in the learning process. Students think natural crystals are very cool as they explore crystallographic topics.

In my Mineralogy course I use single, well-formed crystals in all aspects of basic crystallography including measurement of interfacial angles, determination of symmetry elements, recognition of crystal system and class, determination of forms, stereographic projections and stereograms, recognition of common twins and pseudomorphs, and even SHAPE plots. These are just some of the possibilities.

This approach has a very practical value as well, considering my student population. The mineralogy students I teach are primarily environmental science and education majors, with a few geology majors usually interested in working in the south Texas oil patch. Identifying minerals in hand specimens, aided by a comfortable knowledge of how to recognize crystal system and characteristic crystal shapes, may be one of the most useful crystallographic skills for these students in their later careers.

ACQUISITION OF CRYSTALS

In just the last four years I have purchased euhedral, single crystals of approximately 50 different minerals which I've incorporated into labs and quizzes. I only buy samples whose crystal system and forms can be determined. Most specimens were acquired from dealers at Gem and Mineral shows and rock shops throughout south Texas. (I have been disappointed with specimens purchased sight-unseen through the mail.) If I can assemble a fairly extensive, useful collection of crystals in south Texas, it should be possible to build a similar collection anywhere in the United States.

Many of the best specimens I've purchased are referred to as "thumbnail" size and come in small, clear plastic cases. Some dealers have hundreds of these for sale, often including several of the same mineral from which to choose. Most dealers are also fairly knowledgeable about specific locales of their specimens. Cost varies from a few dollars to a few tens of dollars for larger, more euhedral or less common crystals. Interestingly, single crystals in matrix are also usually more expensive. Many dealers give discounts for college and university purchases. You could start a collection for an investment of just a few hundred dollars, which is less expensive than most other mineralogical supplies and equipment.

COMMONLY AVAILABLE CRYSTALS

All of my crystallography labs are too specific to my collection for reproduction here. Instead, I'll list some crystals you should be able to find, and their commonly available forms:

Isometric System

- Garnet.* (Various species, including Uvarovite)
 - Trapezohedron
 - Dodecahedron
 - Trapezohedron /Dodecahedron combinations (either one dominant)
- Galena.*
 - Cube
 - Cube modified at corners by octahedron
- Magnetite.*
 - Octahedron
- Diamond.*
 - Cube
 - Octahedron
- Halite.*
 - Cube (including hopper crystals)
- Fluorite.*
 - Cube
 - Octahedron (less common)
- Pyrite.*
 - Cube (with and without striations)
 - Cube/Octahedron combinations (either one dominant)
 - Pyritohedron
- Apophyllite.* (Pseudo-isometric)

Hexagonal System

- Beryl.* (Aquamarine and Emerald)
 - Prism with pinacoid
- Molybdenite.*
 - Prism with prominent pinacoid
- Vanadinite.*
 - Prism with prominent pinacoid
- Corundum.*
 - Prism with pinacoid
- Calcite.*
 - Rhombohedron
 - Scalenohedron
- Diopase.*
 - Rhombohedron
- Quartz.*
 - Assorted varieties and forms including scepter crystals, doubly-terminated crystals and enantiomorphic pairs (less common)
- Tourmaline.*
 - Trigonal prism/Hexagonal prism combinations (either one dominant)
 - Trigonal dipyramid with prism
- Benitoite.* Less common, various forms. (Benitoite is the only mineral in the $\bar{6}m2$ class.)
- Aragonite.* (Pseudo-hexagonal cyclic twin)
- Muscovite.* (Pseudo-hexagonal)

Tetragonal System

Vesuvianite.

Dipyramids with prisms and pinacoid

Zircon.

Dipyramid

Dipyramids with prisms

Apophyllite.

Dipyramid with prism

Wulfenite.

Dipyramid with prominent pinacoid

Orthorhombic System

Barite.

Prisms with pinacoid

Danburite.

Prisms with pinacoid

Topaz.

Various combinations of dipyramids with prisms and pinacoid

Monoclinic System

Orthoclase.

Prism with pinacoids

Gypsum.

Prisms with or without pinacoid

Glauberite.

Prism with pinacoid

Triclinic System

These are not common. The only good crystal I have is of relatively rare axinite.

Some minerals, such as native copper, stibnite, smithsonite, wavelite, etc. are rarely found as individual crystals, but are commonly available in crystalline masses that exhibit good examples of habit (dendritic, acicular, botryoidal, radiating, etc.).

SAMPLE QUESTIONS

The number of possible laboratory and quiz questions you can create using real crystals is endless. Some questions are very similar to those you might ask using a good set of wooden or paper models. Other questions are uniquely possible with natural crystals. I also try to relate external crystallinity to atomic structure when possible. I also like to require some sketches of crystals, combining "left brain" and "right brain" activities. Sample questions include:

1. List all symmetry elements present in this crystal.
2. Give the crystal system and class for this crystal.
3. Give the Hermann-Mauguin symbol for this crystal.
4. Sketch the given crystal and list all forms present.
5. Give the form(s) and Miller indices for this crystal.
6. Sketch a face stereogram of this crystal.
7. What are the *general* characteristics of crystals that crystallize in this system?
8. (Various minerals possible)
 - a. Explain the twin law by which this sample is twinned.
 - b. Name the mineral.

9. (For Quartz)
 - a. For each of the given crystals, measure and list the indicated interfacial angles.
 - b. Do size, shape or color of the crystal influence your measurements?
 - c. What is the significance of your measurements?
10. (For Quartz)
 - a. Is this a right-handed or left-handed crystal?
 - b. Give the space group of this crystal.
 - c. Sketch this crystal and identify the trigonal trapezohedral face.
 - d. Discuss the origin of "handedness" in quartz crystals.
11. (For a Quartz scepter crystal)

Explain how this crystal could form.
12. (For Vesuvianite)
 - a. Recreate this crystal using SHAPE and list the parameters.
 - b. Change the parameters and explain how the crystal has changed.
13. (For Staurolite)

Crystals of this mineral, like two of these, are often twinned. Note the third, untwinned crystal. Although actually monoclinic, it appears to be orthorhombic. Explain why.
14. (For cyclically-twinned Aragonite)
 - a. Although aragonite crystallizes in the orthorhombic system, this crystal appears to have the symmetry of what other crystal system?
 - b. Explain why.
15. (For Calcite rhombohedron and scalenohedron, plus several calcite cleavage rhombs)
 - a. Two of these samples are crystals and the others are all cleavage fragments. Pick out the two crystals.
 - b. Explain why this may be difficult.
16. (For Pyrite cube)
 - a. Give the crystal system and class.
 - b. Give the crystal form.
 - c. Explain how this form, which has the symmetry of $4/m\bar{3}2/m$, can exist in this crystal class of lower symmetry.
 - d. Explain the significance of the striations on crystal faces.
17. (For a variety of minerals)
 - a. You have been given a collection of 15 mineral crystals of various shapes, sizes and colors. As an early crystallographer, your job is to create a logical, workable classification scheme for these crystals.
 - b. You have been given 3 additional crystals. Can they be classified within your system, or do you have to modify it? If so, how?

Additional questions can be created for unusual crystals you may find. For example, I have several bixbyite crystals from the Thomas Range, Utah, which are cubes modified at the corners by a trapezohedron. The trapezohedron can only be identified by sketching a face stereogram, as the shape of the three faces at the corners superficially resemble faces of a trisoctahedron.

CONCLUSIONS

The extensive use of euhedral, single, natural mineral crystals is a very low-tech and low-cost approach to teaching basic concepts of crystallography. I have found that this approach makes the entire subject of crystallography much more real and accessible to students. Students prefer working with these crystals rather than the traditional wooden or paper models, an enthusiasm which seems to carry over into other classroom topics and laboratory exercises.

THE METRICAL MATRIX IN TEACHING MINERALOGY

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INTRODUCTION

The calculation of the d -spacings, the angles between planes and zones, the bond lengths and angles and other important geometric relationships for a mineral can be a tedious task both for the student and the instructor, particularly when completed with the large assortment of trigonometric identities and algebraic formulae that are available (cf. Crystal Geometry (1959), Donnay and Donnay, International Tables for Crystallography, Vol. II, Section 3, The Kynoch Press, 101–158). However, such calculations are straightforward and relatively easy to do when completed with the metrical matrix and the interactive software MATOP. Several applications of the matrix are presented below, each of which is worked out in detail and which is designed to teach you its use in the study of crystal geometry.

SOME PRELIMINARY COMMENTS

We begin our discussion of the matrix with a brief examination of the properties of the geometric three dimensional space, S , in which we live and in which minerals and rocks occur. For our purposes, it will be convenient to view S as the set of all vectors that radiate from a common origin to each point in space. In constructing a model for S , we chose three noncoplanar, coordinate axes denoted X , Y and Z , each radiating from the origin, $\mathbf{0}$. Next, we place three nonzero vectors denoted \mathbf{a} , \mathbf{b} and \mathbf{c} along X , Y and Z , respectively, likewise radiating from $\mathbf{0}$. Since the vectors $D = \{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$ are nonzero, noncoplanar vectors, they qualify as basis vectors for S . This means that for each vector \mathbf{v} in S there exist three real numbers x , y and z such that \mathbf{v} can be written uniquely as $\mathbf{v} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$.

In the study of minerals, the coordinate X -, Y - and Z -axes and the basis vectors are chosen to coincide with three intersecting, noncoplanar edges of a representative block (parallelepiped) of the crystal structure called the unit cell. The magnitudes (lengths) of the basis vectors, \mathbf{a} , \mathbf{b} and \mathbf{c} , denoted a , b and c , respectively, are each taken as equal to the lengths of the three edges of the cell. In many cases, the cell edges are different in length such that $a \neq b \neq c$. The angles between the basis vectors $\alpha = \angle \mathbf{b} \wedge \mathbf{c}$, $\beta = \angle \mathbf{a} \wedge \mathbf{c}$ and $\gamma = \angle \mathbf{a} \wedge \mathbf{b}$ are taken as the interaxial angles; angles other than 90° , 60° , 120° , 109.47° etc., are often encountered. (cf. Fig 2.3, MSA Reviews in Mineralogy, Vol. 15, by Boisen and Gibbs, 1990 (B&G)). Once the size, shape and orientation of a unit cell is determined in an X-ray diffraction experiment, the choice of the origin, the coordinates axes and the basis vectors for a mineral is completely determined.

As it is difficult to enter a directed line segment \mathbf{v} directly into a computer, a correspondence is established between each vector $\mathbf{v} \in S$ and its triple representative $[\mathbf{v}]_D$. A set of three real numbers x , y and z form a triple representation of each vector $\mathbf{v} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c} \in S$ symbolized as

$$\mathbf{v} \Longleftrightarrow [\mathbf{v}]_D = \begin{bmatrix} x \\ y \\ z \end{bmatrix}.$$

As the components of the triple are real numbers, they can be easily read into the computer or used in a calculation with a hand-held calculator (B&G, 21–25).

In most math courses, S is usually defined in terms of the well-known Cartesian basis $C = \{\mathbf{i}, \mathbf{j}, \mathbf{k}\}$ such that each vector $\mathbf{v} \in S$ can be written uniquely as $\mathbf{v} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$ where x, y and z are again real numbers. The triple representative for a vector \mathbf{v} , written in terms of the C -basis, is denoted as

$$[\mathbf{v}]_C = \begin{bmatrix} x \\ y \\ z \end{bmatrix}.$$

Although the components of the triples $[\mathbf{v}]_C$ and $[\mathbf{v}]_D$ are identical in appearance, the subscripts tell us that they can represent quite different vectors in S , one written in terms of the C -basis and the other in terms of the D -basis. When we use these components in a calculation or enter them into a computer, we require a metrical matrix, denoted G , that completely characterizes the geometry of the basis vectors and makes the arithmetic come out right regardless of whether one is using the natural basis in studying minerals or the Cartesian basis in studying mathematics.

The metrical matrix is found by evaluating the inner (dot) product of the nonzero vectors

$$\mathbf{v} = v_1\mathbf{a} + v_2\mathbf{b} + v_3\mathbf{c} \quad \text{and} \quad \mathbf{w} = w_1\mathbf{a} + w_2\mathbf{b} + w_3\mathbf{c}$$

where the product, denoted $\mathbf{v} \cdot \mathbf{w}$, is defined to be $\mathbf{v} \cdot \mathbf{w} = vw \cos \theta$, where θ is the angle between \mathbf{v} and \mathbf{w} such that $0^\circ \leq \theta \leq 180^\circ$ and where v and w are the lengths of \mathbf{v} and \mathbf{w} , respectively. Hence, the angle between the two vectors is given by the expression $\cos \theta = (\mathbf{v} \cdot \mathbf{w})/(vw)$. The length of a vector \mathbf{v} , for example, is found by forming the inner product $\mathbf{v} \cdot \mathbf{v} = v^2 \cos 0^\circ = v^2$. When written in terms of the triple representative of \mathbf{v} , $[\mathbf{v}]_D$ (cf. B&G, 25-28),

$$\mathbf{v} \cdot \mathbf{v} = v^2 = [\mathbf{v}]_D^t G [\mathbf{v}]_D$$

where

$$G = \begin{bmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ab \cos \gamma & b^2 & bc \cos \alpha \\ ac \cos \beta & bc \cos \alpha & c^2 \end{bmatrix}$$

and where $[\mathbf{v}]_D^t = [v_1 \ v_2 \ v_3]$ and $[\mathbf{v}]_D = \begin{bmatrix} v_1 \\ v_2 \\ v_3 \end{bmatrix}$. By evaluating $(\mathbf{v} \cdot \mathbf{v})^{1/2} = ([\mathbf{v}]_D^t G [\mathbf{v}]_D)^{1/2}$, the length of the vector \mathbf{v} is found. Likewise, $\mathbf{v} \cdot \mathbf{w} = [\mathbf{v}]_D^t G [\mathbf{w}]_D$ and since

$$\mathbf{v} \cdot \mathbf{w} = vw \cos \theta = ([\mathbf{v}]_D^t G [\mathbf{v}]_D)^{1/2} ([\mathbf{w}]_D^t G [\mathbf{w}]_D)^{1/2} \cos \theta = [\mathbf{v}]_D^t G [\mathbf{w}]_D,$$

it follows that

$$\cos \theta = \frac{([\mathbf{v}]_D^t G [\mathbf{w}]_D)}{([\mathbf{v}]_D^t G [\mathbf{v}]_D)^{1/2} ([\mathbf{w}]_D^t G [\mathbf{w}]_D)^{1/2}}$$

where $[\mathbf{v}]_D^t = [v_1 \ v_2 \ v_3]$, $[\mathbf{w}]_D^t = [w_1 \ w_2 \ w_3]$, $[\mathbf{v}]_D = \begin{bmatrix} v_1 \\ v_2 \\ v_3 \end{bmatrix}$ and $[\mathbf{w}]_D = \begin{bmatrix} w_1 \\ w_2 \\ w_3 \end{bmatrix}$.

For a Cartesian basis, the metrical matrix G is equal to the identity matrix I_3 ; $G = I_3$ because \mathbf{i}, \mathbf{j} and \mathbf{k} are mutually perpendicular, unit length vectors. Hence, the inner product of a vector $\mathbf{v} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$, written in terms of a Cartesian basis, becomes

$$\mathbf{v} \cdot \mathbf{v} = [\mathbf{v}]_C^t I_3 [\mathbf{v}]_C = \begin{bmatrix} x & y & z \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x & y & z \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = x^2 + y^2 + z^2.$$

As indicated above, a unit cell, an origin, a set of basis vectors and a coordinate system is defined, in a crystal structure analysis, in a natural way for each mineral. Without these constructs and the model for S , the study of the geometry and symmetry of minerals becomes a qualitative chore, providing little meaningful insight into the nature of their properties and their possible uses. The C -basis is not without its use in studying minerals. For example, it can be used to generate the ϕ and ρ angles for plotting face poles and zones in stereographic projection (cf. B&G, 75–83).

Miller indices, zone axes and the positions of the atoms in the unit cell are defined in terms of the basis vectors and the coordinate system that correspond with those of the lattice representation, L_D , of the periodic symmetry of a mineral. Mineralogy students are often taught this but they may not appreciate the full power and convenience of basis vectors unless they attempt to calculate the angular and spatial relationships that exists among the faces and zones for a triclinic mineral like kyanite. In this note, a number of worked examples of useful crystallographic calculations are presented that could be included in mineralogy lectures or homework assignments. If you would like to convince your students that unit cells, zones and Miller indices are really useful, read on. In the pages that follow, interzonal and interfacial angles, $d_{(hkl)}$ -spacings, bond lengths and angles and unit cell volumes are calculated, each with the metrical matrix. The calculations entail adding, subtracting and multiplying vectors and matrices (evaluating inner products). These are relatively simple operations for a system defined in terms of a Cartesian basis and surprisingly straightforward operations when completed for the natural basis of a mineral. The derivation of the expressions used in this note together with a number of additional problems and examples can be found in B&G. Also, a review of matrices and determinants and the rules of matrix multiplication and matrix inversion are given in Appendix 2 of B&G or in almost any text on linear algebra.

As is well-known, crystallographic calculations are usually time consuming and open to error when completed by hand or with a calculator. To avoid these problems, the program MATOP was written for our students at Virginia Tech and for anyone else who has need of it. MATOP is an interactive program that begins by asking the user for the cell dimensions of a mineral. It then proceeds by calculating the metrical matrix G and its inverse, G^{-1} . Up to three 3×3 matrices can be entered into MATOP. Upon request, it multiplies and inverts these matrices including the metrical matrix, it multiplies a matrix by a triple (a vector), it evaluates inner and cross products of vectors, etc. With MATOP, the problems in this note and those in B&G can be completed rapidly and with little effort (See Boisen, Jr., M.B. and G.V. Gibbs, (1988), *MATOP: An interactive FORTRAN 77 Program for Solving Problems in Geometrical Crystallography*. Computers & Geosciences, 14, 37-53; problems similar to those worked here as well as others are solved step by step in this paper with MATOP). The note ends with a brief discussion of the connection that exist between the periodic crystal structure of a mineral and its lattice representation together with a discussion of the connection that exists between planes and lines of the lattice and faces and zones of the mineral. A simple rule is given that can be used to find the equation of a lattice (crystal) plane and its Miller indices.

APPLICATIONS OF THE METRICAL MATRIX

EXAMPLE 1: Constructing a metrical matrix

Suppose that the unit cell dimensions of a triclinic rhodonite crystal are $a = 10.497\text{\AA}$, $b = 9.797\text{\AA}$, $c = 12.185\text{\AA}$, $\alpha = 103.00^\circ$, $\beta = 108.51^\circ$ and $\gamma = 82.50^\circ$. With this information, the metrical matrix becomes

$$G = \begin{bmatrix} 110.187009 & 13.423197 & -40.606321 \\ 13.423197 & 95.981209 & -26.853857 \\ -40.606321 & -26.853857 & 148.474225 \end{bmatrix}.$$

PROBLEM 1: Calculate the metrical matrix for an orthorhombic crystal with cell dimensions $a = 3.397\text{\AA}$, $b = 11.321\text{\AA}$, $c = 6.516\text{\AA}$, $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$ and $\gamma = 90.00^\circ$.

SOLUTION

$$G = \begin{bmatrix} 11.539609 & 0.0 & 0.0 \\ 0.0 & 128.165041 & 0.0 \\ 0.0 & 0.0 & 42.458256 \end{bmatrix}$$

DEFINITION 1: An expression for calculating the angle between two zones

Suppose that $[u_1 \ v_1 \ w_1]$ and $[u_2 \ v_2 \ w_2]$ are the indices of two zones defined by the vectors $\mathbf{r}_1 = u_1\mathbf{a} + v_1\mathbf{b} + w_1\mathbf{c}$ and $\mathbf{r}_2 = u_2\mathbf{a} + v_2\mathbf{b} + w_2\mathbf{c}$, respectively, in a crystal, then the angle δ between the two is given by the expression

$$\cos \delta = \mathbf{r}_1 \cdot \mathbf{r}_2 / (r_1 r_2) = \frac{([\mathbf{r}_1]_D^t G [\mathbf{r}_2]_D)}{([\mathbf{r}_1]_D^t G [\mathbf{r}_1]_D)^{1/2} ([\mathbf{r}_2]_D^t G [\mathbf{r}_2]_D)^{1/2}}.$$

EXAMPLE 2: A calculation of the angle between two zones

Given the unit cell dimensions for rhodonite (Example 1), calculate the angle δ between the zones $[-1 \ 1 \ 2]$ and $[2 \ 1 \ 3]$. To find the angle, the following three expressions are evaluated: $([\mathbf{r}_1]_D^t G [\mathbf{r}_2]_D)$, $([\mathbf{r}_1]_D^t G [\mathbf{r}_1]_D)^{1/2}$ and $([\mathbf{r}_2]_D^t G [\mathbf{r}_2]_D)^{1/2}$. Setting $[\mathbf{r}_1]_D^t = [u_1 \ v_1 \ w_1] = [-1 \ 1 \ 2]$ and $[\mathbf{r}_2]_D^t = [u_2 \ v_2 \ w_2] = [2 \ 1 \ 3]$, we can write

$$([\mathbf{r}_1]_D^t G [\mathbf{r}_2]_D) = [-1 \ 1 \ 2] \begin{bmatrix} 110.187009 & 13.423197 & -40.606321 \\ 13.423197 & 95.981209 & -26.853857 \\ -40.606321 & -26.853857 & 148.474225 \end{bmatrix} \begin{bmatrix} 2 \\ 1 \\ 3 \end{bmatrix} =$$

$$[-1 \ 1 \ 2] \begin{bmatrix} 111.9782508 \\ 42.2660321 \\ 337.3561748 \end{bmatrix} = 605.000131,$$

$$([\mathbf{r}_1]_D^t G [\mathbf{r}_1]_D) = [-1 \ 1 \ 2] \begin{bmatrix} 110.187009 & 13.423197 & -40.606321 \\ 13.423197 & 95.981209 & -26.853857 \\ -40.606321 & -26.853857 & 148.474225 \end{bmatrix} \begin{bmatrix} -1 \\ 1 \\ 2 \end{bmatrix} =$$

$$[-1 \ 1 \ 2] \begin{bmatrix} -177.9764547 \\ 28.8502974 \\ 310.7009143 \end{bmatrix} = 828.228581,$$

$$([\mathbf{r}_2]_D^t G [\mathbf{r}_2]_D) = [2 \ 1 \ 3] \begin{bmatrix} 110.187009 & 13.423197 & -40.606321 \\ 13.423197 & 95.981209 & -26.853857 \\ -40.606321 & -26.853857 & 148.474225 \end{bmatrix} \begin{bmatrix} 2 \\ 1 \\ 3 \end{bmatrix} =$$

$$[2 \ 1 \ 3] \begin{bmatrix} 111.9782508 \\ 42.2660321 \\ 337.3561748 \end{bmatrix} = 1278.291058.$$

Recalling that

$$\cos \delta = \frac{([\mathbf{r}_1]_D^t G [\mathbf{r}_2]_D)}{([\mathbf{r}_1]_D^t G [\mathbf{r}_1]_D)^{1/2} ([\mathbf{r}_2]_D^t G [\mathbf{r}_2]_D)^{1/2}},$$

$$\cos \delta = \frac{605.000131}{(828.228581)^{1/2} (1278.29105)^{1/2}} = 0.587984.$$

Hence, $\delta = 53.99^\circ$.

PROBLEM 2: Calculate the angle between the zones $[1 \ -1 \ 2]$ and $[3 \ 1 \ 1]$ for the orthorhombic crystal described in Problem 1.

SOLUTION

91.70°

DEFINITION 2: An expression for calculating $d_{(hkl)}$ -spacings

Given the indices h, k and l of a lattice plane and a set of unit cell dimensions, the $d_{(hkl)}$ -spacing of the plane can be found with the quadratic expression

$$Q_{(hkl)} = 1/d_{hkl}^2 = [\mathbf{s}]_{D^*}^t \mathbf{G}^{-1} [\mathbf{s}]_{D^*}$$

where $[\mathbf{s}]_{D^*}^t = [h \ k \ l]$ and $[\mathbf{s}]_{D^*} = \begin{bmatrix} h \\ k \\ l \end{bmatrix}$. Hence, it follows that

$$1/d_{(hkl)}^2 = [h \ k \ l] \begin{bmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ab \cos \gamma & b^2 & bc \cos \alpha \\ ac \cos \beta & bc \cos \alpha & c^2 \end{bmatrix}^{-1} \begin{bmatrix} h \\ k \\ l \end{bmatrix}.$$

The subscript D^* denotes an important set of basis vectors $D^* = \{\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*\}$ defined on S that play a central role in the interpretation of the X-diffraction record of a mineral and the solution of its crystal structure. The geometry of the D^* -basis is completely defined by $\mathbf{G}^* = \mathbf{G}^{-1}$ just as that of the D -basis is defined by \mathbf{G} . It is important to note that there exists a vector $\mathbf{s} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ perpendicular to each potential plane (hkl) of a mineral. In addition, the vector \mathbf{s} has the length $s = 1/d_{(hkl)}$ such that the inner product $\mathbf{s} \cdot \mathbf{s} = 1/d_{(hkl)}^2 = [\mathbf{s}]_{D^*}^t \mathbf{G}^* [\mathbf{s}]_{D^*}$. The reciprocal metrix matrix

$$\mathbf{G}^* = \begin{bmatrix} a^{*2} & a^*b^* \cos \gamma^* & a^*c^* \cos \beta^* \\ a^*b^* \cos \gamma^* & b^{*2} & b^*c^* \cos \alpha^* \\ a^*c^* \cos \beta^* & b^*c^* \cos \alpha^* & c^{*2} \end{bmatrix}$$

completely defines the geometry of the reciprocal lattice, L_{D^*} , just as \mathbf{G} defines the geometry of the direct lattice, L_D .

EXAMPLE 3: A calculation of a $d_{(hkl)}$ -spacing

Given the cell dimensions for kyanite $a = 7.126\text{\AA}$, $b = 7.852\text{\AA}$, $c = 5.572\text{\AA}$, $\alpha = 89.99^\circ$, $\beta = 101.11^\circ$ and $\gamma = 106.03^\circ$, calculate the d -spacing for the plane $(2 \ -3 \ 1)$.

SOLUTION

As defined above,

$$1/d_{(hkl)}^2 = [h \ k \ l] \begin{bmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ab \cos \gamma & b^2 & bc \cos \alpha \\ ac \cos \beta & bc \cos \alpha & c^2 \end{bmatrix}^{-1} \begin{bmatrix} h \\ k \\ l \end{bmatrix}.$$

Replacing the entries of the matrix with the given cell dimensions and h, k and l by 2, -3 and 1, respectively, we have

$$1/d_{(2-31)}^2 = [2 \ -3 \ 1] \begin{bmatrix} 50.779876 & -15.450994 & -7.651091 \\ -15.450994 & 61.653904 & 0.007636 \\ -7.651091 & 0.007636 & 31.047184 \end{bmatrix}^{-1} \begin{bmatrix} 2 \\ -3 \\ 1 \end{bmatrix}.$$

Next, inverting the G matrix to obtain G^{-1} ,

$$\begin{aligned} 1/d_{(2-31)}^2 &= \begin{bmatrix} 2 & -3 & 1 \end{bmatrix} \begin{bmatrix} 0.022211 & 0.005566 & 0.005472 \\ 0.005566 & 0.017614 & 0.001367 \\ 0.005472 & 0.001367 & 0.033557 \end{bmatrix} \begin{bmatrix} 2 \\ -3 \\ 1 \end{bmatrix} = \\ & \begin{bmatrix} 2 & -3 & 1 \end{bmatrix} \begin{bmatrix} 0.0331971 \\ -0.0403442 \\ 0.0403999 \end{bmatrix} = 0.22783. \end{aligned}$$

Hence, $d_{(2-31)} = 2.095\text{\AA}$.

PROBLEM 3: Calculate the $d_{(123)}$ -spacing for the plane (123) for the orthorhombic crystal discussed in Problem 1.

SOLUTION

$$d_{(123)} = 1.741\text{\AA}$$

DEFINITION 3: An expression for calculating the angle between two face poles.

Suppose that (h_1, k_1, l_1) and (h_2, k_2, l_2) are two planes of a crystal, then the angle, Δ , between the poles to these faces is given by the expression

$$\cos \Delta = \frac{([s_1]_{D^*}^t G^{-1} [s_2]_{D^*})}{([s_1]_{D^*}^t G^{-1} [s_1]_{D^*})^{1/2} ([s_2]_{D^*}^t G^{-1} [s_2]_{D^*})^{1/2}}$$

$$\text{where } [s_1]_{D^*}^t = [h_1 \ k_1 \ l_1], [s_2]_{D^*}^t = [h_2 \ k_2 \ l_2], [s_1]_{D^*} = \begin{bmatrix} h_1 \\ k_1 \\ l_1 \end{bmatrix} \text{ and } [s_2]_{D^*} = \begin{bmatrix} h_2 \\ k_2 \\ l_2 \end{bmatrix}.$$

EXAMPLE 4: Calculation of the interfacial angle between two planes

The structure of kyanite can be viewed as based on a cubic close-packed array of oxide anions with close-packed monolayers layers paralleling (110), (-122) , $(0-11)$ and $(3-20)$ (cf. B&G, 65-71). Determine the interfacial angle Δ between the planes (-122) and $(3-20)$.

SOLUTION

Our task is to evaluate

$$\cos \Delta = \frac{([s_1]_{D^*}^t G^{-1} [s_2]_{D^*})}{([s_1]_{D^*}^t G^{-1} [s_1]_{D^*})^{1/2} ([s_2]_{D^*}^t G^{-1} [s_2]_{D^*})^{1/2}}$$

which is done by evaluating $[s_1]_{D^*}^t G^{-1} [s_2]_{D^*}$, $([s_1]_{D^*}^t G^{-1} [s_1]_{D^*})^{1/2}$ and $([s_2]_{D^*}^t G^{-1} [s_2]_{D^*})^{1/2}$. With $h_1 = -1$, $k_1 = 2$, $l_1 = 2$, $h_2 = 3$, $k_2 = -2$ and $l_2 = 0$ and with the cell dimensions of kyanite (Example 3),

$$[s_1]_{D^*}^t G^{-1} [s_1]_{D^*} = \begin{bmatrix} -1 & 2 & 2 \end{bmatrix} \begin{bmatrix} 50.779876 & -15.450994 & -7.651091 \\ -15.450994 & 61.653904 & 0.007636 \\ -7.651091 & 0.007636 & 31.047184 \end{bmatrix}^{-1} \begin{bmatrix} -1 \\ 2 \\ 2 \end{bmatrix}.$$

Next, inverting the G matrix,

$$[s_1]_{D^*}^t G^{-1} [s_1]_{D^*} = \begin{bmatrix} -1 & 2 & 2 \end{bmatrix} \begin{bmatrix} 0.022211 & 0.005566 & 0.005472 \\ 0.005566 & 0.017614 & 0.001367 \\ 0.005472 & 0.001367 & 0.033557 \end{bmatrix} \begin{bmatrix} -1 \\ 2 \\ 2 \end{bmatrix} = 0.193683,$$

$$[s_2]_{D^*}^t G^{-1} [s_2]_{D^*} = \begin{bmatrix} 3 & -2 & 0 \end{bmatrix} \begin{bmatrix} 0.022211 & 0.005566 & 0.005472 \\ 0.005566 & 0.017614 & 0.001367 \\ 0.005472 & 0.001367 & 0.033557 \end{bmatrix} \begin{bmatrix} 3 \\ -2 \\ 0 \end{bmatrix} = 0.203567,$$

$$[s_2]_{D^*}^t G^{-1} [s_2]_{D^*} = \begin{bmatrix} -1 & 2 & 2 \end{bmatrix} \begin{bmatrix} 0.022211 & 0.005566 & 0.005472 \\ 0.005566 & 0.017614 & 0.001367 \\ 0.005472 & 0.001367 & 0.033557 \end{bmatrix} \begin{bmatrix} 3 \\ -2 \\ 0 \end{bmatrix} = -0.065201.$$

Hence, $\cos \Delta = -0.065201 / ((0.193683)^{1/2} \times (0.203567)^{1/2})$ and $\Delta = 109.17^\circ$. This angle is closed to the ideal tetrahedra angle of 109.47° that would have obtained if the oxide anions in the kyanite structure were ideally cubic close-packed.

PROBLEM 4: Calculate the angle between the close-packed monolayers of oxide anions that parallel (-122) and $(3-20)$ in kyanite.

SOLUTION

$$\Delta = 109.17^\circ$$

DEFINITION 4: An expression for calculating the angle between a face pole and a zone

The angle, ϵ , between a face pole (hkl) and a zone $[uvw]$ is given by the expression

$$\cos \epsilon = \frac{[s]_{D^*}^t [r]_D}{([s]_{D^*}^t G^{-1} [s]_{D^*})^{1/2} ([r]_D^t G [r]_D)^{1/2}}$$

where $[s]_{D^*}^t = [h \ k \ l]$ and $[r]_D = \begin{bmatrix} u \\ v \\ w \end{bmatrix}$.

EXAMPLE 5: Calculation of the angle between a zone and a face pole

Calculate the angle, ϵ , between the close-packed plane $(-1 \ 2 \ 2)$ and the zone $[8 \ 7 \ 2]$ of kyanite where $[8 \ 7 \ 2]$ defines a zone that is perpendicular to one of the oxide monolayers in the cubic close-packed structure. The angle is given by the expression

$$\cos \epsilon = \frac{hu + kv + lw}{([s]_{D^*}^t G^{-1} [s]_{D^*})^{1/2} ([r]_D^t G [r]_D)^{1/2}}$$

SOLUTION

$$\cos \epsilon = \frac{10}{(0.193883)^{1/2} (4420.009648)^{1/2}} = 0.341601$$

and $\epsilon = 70.03^\circ$. This angle is close to the ideal angle of 70.53° expected between a vector perpendicular to an oxide anion monolayer and another monolayer in a cubic close-packed structure.

PROBLEM 5: Calculate the angle between the monolayer of oxide anions that parallels the $(1 \ 1 \ 0)$ plane and the $[0 \ 1 \ 2]$ zone in kyanite.

SOLUTION

71.04°

DEFINITION 5: An expression for calculating the unit cell volume

The volume v of the unit cell is given by the expression

$$v^2 = \det G = a^2 b^2 c^2 (1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma).$$

EXAMPLE 6: Calculation of the volume of the unit cell

Given that the cell dimensions of coesite, a high pressure monoclinic form of silica, are $a = 7.135 \text{ \AA}$, $b = 12.372 \text{ \AA}$, $c = 7.173 \text{ \AA}$, $\alpha = \gamma = 90^\circ$ and $\beta = 120.36^\circ$, calculate the volume of its unit cell. The unit cell volume of coesite is obtained using the expression

$$v^2 = \det G = \det \begin{bmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ab \cos \gamma & b^2 & bc \cos \alpha \\ ac \cos \beta & bc \cos \alpha & c^2 \end{bmatrix}$$

which for coesite becomes

$$\det \begin{bmatrix} 50.908225 & 0.0 & -25.867658 \\ 0.0 & 153.066384 & 0.0 \\ -25.867658 & 0.0 & 51.45192 \end{bmatrix} =$$

$$153.066384(50.908225 \times 51.45192 - 25.867658 \times 25.867658) = (546.36)^2 \text{ \AA}^6$$

Hence, the volume of the unit cell of coesite is $v = 546.36 \text{ \AA}^3$.

PROBLEM 6: Calculate the volume of the unit cell in quartz given that $a = b = 4.914 \text{ \AA}$, $c = 5.409 \text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$.

SOLUTION

$$113.114 \text{ \AA}^3$$

BOND LENGTH AND ANGLE CALCULATIONS

A close connection exists between crystal chemistry of a mineral and the bond lengths and angles exhibited by its crystal structure. Indeed, a knowledge of the bond lengths and angles is necessary for determining the likely coordination numbers of the atoms, for a description of the structure and for an understanding of certain physical properties. This example illustrates how the SiO bond lengths in two corner sharing silicate tetrahedra and the SiOSi angle that links the tetrahedra into a chain in pectolite can be calculated with the metrical matrix. The cell dimensions of pectolite are $a = 7.988 \text{ \AA}$, $b = 7.040 \text{ \AA}$, $c = 7.025 \text{ \AA}$, $\alpha = 90.51^\circ$, $\beta = 95.18^\circ$ and $\gamma = 102.47^\circ$. A structure analysis of the mineral shows that the fractional positional coordinates (x, y, z) of the two Si atoms, (denoted Si₂ and Si₃) are (0.2150, 0.9544, 0.3440) and (0.4505, 0.7353, 0.1447), respectively, while that of the O atom (denoted O₈) is (0.3955, 0.9092, 0.2746). In this example, the separations (bond lengths) between Si₂ and O₈ and Si₃ and O₈ and the Si₂O₈Si₃ angle are calculated. The two bond lengths, denoted $R(\text{Si}_2\text{O}_8)$ and $R(\text{Si}_3\text{O}_8)$, are calculated below in three steps followed by a calculation of the angle.

EXAMPLE 7: Calculation of SiO bond lengths

Step 1: Calculation of the metrical matrix for pectolite:

$$G = \begin{bmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ab \cos \gamma & b^2 & bc \cos \alpha \\ ac \cos \beta & bc \cos \alpha & c^2 \end{bmatrix} = \begin{bmatrix} 63.808144 & -12.142846 & -5.066403 \\ -12.142846 & 49.561600 & -0.440211 \\ -5.066403 & -0.440211 & 49.350625 \end{bmatrix}$$

Step 2: If we denote the vectors that radiate from the origin of the unit cell, $\mathbf{0}$, to O_8 , Si_2 and Si_3 , to be \mathbf{v}_1 , \mathbf{v}_2 and \mathbf{v}_3 respectively, and those that radiate from O_8 to Si_2 and Si_3 to be \mathbf{v}_4 and \mathbf{v}_5 , respectively, then the lengths of the Si_2O_8 and the Si_3O_8 bonds are equal to $|\mathbf{v}_4|$ and $|\mathbf{v}_5|$, respectively. The triple representatives of these vectors are:

$$[\mathbf{v}_1]_D = \begin{bmatrix} 0.3955 \\ 0.9092 \\ 0.2746 \end{bmatrix}, [\mathbf{v}_2]_D = \begin{bmatrix} 0.2150 \\ 0.9544 \\ 0.3440 \end{bmatrix} \text{ and } [\mathbf{v}_3]_D = \begin{bmatrix} 0.4505 \\ 0.7353 \\ 0.1447 \end{bmatrix},$$

$$[\mathbf{v}_4]_D = [\mathbf{v}_2]_D - [\mathbf{v}_1]_D = \begin{bmatrix} 0.2150 \\ 0.9544 \\ 0.3440 \end{bmatrix} - \begin{bmatrix} 0.3955 \\ 0.9092 \\ 0.2746 \end{bmatrix} = \begin{bmatrix} -0.1805 \\ 0.0452 \\ 0.0694 \end{bmatrix} \text{ and}$$

$$[\mathbf{v}_5]_D = [\mathbf{v}_3]_D - [\mathbf{v}_1]_D = \begin{bmatrix} 0.4505 \\ 0.7353 \\ 0.1447 \end{bmatrix} - \begin{bmatrix} 0.3955 \\ 0.9092 \\ 0.2746 \end{bmatrix} = \begin{bmatrix} 0.0550 \\ -0.1739 \\ -0.1299 \end{bmatrix}.$$

Step 3: With the triples for $[\mathbf{v}_4]_D$ and $[\mathbf{v}_5]_D$ and the metrical matrix G , we can write the equality

$$\begin{aligned} |\mathbf{v}_4|^2 &= R(\text{Si}_2\text{O}_8)^2 = [\mathbf{v}_4]_D^t G [\mathbf{v}_4]_D = \\ &= \begin{bmatrix} -0.1805 & 0.0452 & 0.0694 \end{bmatrix} \begin{bmatrix} 63.808144 & -12.142846 & -5.066403 \\ -12.142846 & 49.561600 & -0.440211 \\ -5.066403 & -0.440211 & 49.350625 \end{bmatrix} \begin{bmatrix} -0.1805 \\ 0.0452 \\ 0.0694 \end{bmatrix} \\ &= \begin{bmatrix} -0.1805 & 0.0452 & 0.0694 \end{bmatrix} \begin{bmatrix} -12.4178350 \\ 4.4014173 \\ 4.3195216 \end{bmatrix} = (1.655336)^2. \end{aligned}$$

$$\begin{aligned} |\mathbf{v}_5|^2 &= R(\text{Si}_3\text{O}_8)^2 = [\mathbf{v}_5]_D^t G [\mathbf{v}_5]_D = \\ &= \begin{bmatrix} 0.0550 & -0.1739 & -0.1299 \end{bmatrix} \begin{bmatrix} 63.808144 & -12.142846 & -5.066403 \\ -12.142846 & 49.561600 & -0.440211 \\ -5.066403 & -0.440211 & 49.350625 \end{bmatrix} \begin{bmatrix} 0.0550 \\ -0.1739 \\ -0.1299 \end{bmatrix} \\ &= \begin{bmatrix} 0.0550 & -0.1739 & -0.1299 \end{bmatrix} \begin{bmatrix} 6.2792145 \\ -9.2294354 \\ -6.6127457 \end{bmatrix} = (1.676112)^2 \text{ and} \end{aligned}$$

hence, the lengths of the Si_2O_8 and Si_3O_8 bonds are 1.655\AA and 1.676\AA , respectively.

EXAMPLE 8: A calculation of the SiOSi angle

Step 1. The SiOSi angle is calculated with the expression

$$\cos \angle (\text{Si}_3\text{O}_8\text{Si}_2) = ([\mathbf{v}_5]_D^t G [\mathbf{v}_4]_D) / ([[\mathbf{v}_5]_D^t G [\mathbf{v}_5]_D]^{1/2} ([\mathbf{v}_4]_D^t G [\mathbf{v}_4]_D)^{1/2}) =$$

$$([\mathbf{v}_5]_D^t G[\mathbf{v}_4]_D) / (R(\text{Si}_3\text{O}_8) \times R(\text{Si}_2\text{O}_8)).$$

We next evaluate

$$([\mathbf{v}_5]_D^t G[\mathbf{v}_4]_D),$$

and obtain

$$\begin{bmatrix} 0.0550 & -0.1739 & -0.1299 \end{bmatrix} \begin{bmatrix} 63.808144 & -12.142846 & -5.066403 \\ -12.142846 & 49.561600 & -0.440211 \\ -5.066403 & -0.440211 & 49.350625 \end{bmatrix} \begin{bmatrix} -0.1805 \\ 0.0452 \\ 0.0694 \end{bmatrix} = -2.009493.$$

Hence,

$$\cos < (\text{Si}_3\text{O}_8\text{Si}_2) = -2.009493 / (1.676112 \times 1.655336)$$

from which it follows that

$$< (\text{Si}_3\text{O}_8\text{Si}_2) = 136.408^\circ.$$

PROBLEM 7: Calculate the Si_1O_3 and the Si_1O_4 bond lengths and the $\text{O}_3\text{Si}_1\text{O}_4$ angle for coesite given that $a = 7.1367\text{\AA}$, $b = 12.3695\text{\AA}$, $c = 7.1742\text{\AA}$, $\alpha = \gamma = 90^\circ$ and $\beta = 120.337^\circ$ and that the fraction coordinates of Si_1 , O_3 and O_4 are $(0.14034, 0.10832, 0.07233)$, $(0.26628, 0.12309, -0.05990)$ and $(0.31097, 0.10374, 0.32799)$, respectively.

SOLUTION

$$R(\text{Si}_1\text{O}_3) = 1.613\text{\AA}; R(\text{Si}_1\text{O}_4) = 1.611\text{\AA}; <\text{O}_3\text{Si}_1\text{O}_4 = 110.38^\circ$$

CRYSTAL FACES, LATTICE PLANES AND MILLER INDICES

Lattices play a fundamental role in the study of crystals in that they can be used to represent the translational symmetry and the periodic structure of a crystal. For our purposes, a crystal can be defined as an array of bonded atoms that repeats at regular intervals along parallel lines in S . By replacing each such array of atoms by a lattice point, a 3D lattice L_D results. In other words, a lattice is an array of lattice points that repeats at regular intervals along parallel lines in S . As the points in a lattice are all translationally equivalent, the environment about each array of atoms represented by a lattice point is identical to each other such array in the crystal.

Each plane of lattice points (lattice plane) in L_D parallels a potential face on a crystal and each line of lattice points parallels the line formed by two or more such intersecting lattice (crystal) planes. As lattice (crystal) planes and their lines of intersection are defined by lattice points in S , they are defined by sets of three integers referred to as indices. The line formed by the intersection of two or more nonparallel lattice planes is called a zone denoted $[uvw]$ where u, v and w are integers (zone indices), while the lattice planes themselves are defined by three integers (hkl) , referred to as the Miller indices of the plane.

EXAMPLE 9: A derivation of the equation of a lattice (crystal) plane and its Miller indices

RULE: Suppose that the expression $v_1x + v_2y + v_3z = 1$ defines a plane in S where x, y and z are indeterminants and v_1, v_2 and v_3 are real numbers. If the end point of a vector $\mathbf{v} = p\mathbf{a} + q\mathbf{b} + r\mathbf{c}$ lies on a plane P , then the equation of the plane is found by simply replacing the indeterminates x, y and z in the expression $v_1x + v_2y + v_3z = 1$ by p, q and r , respectively, to yield the equation $v_1p + v_2q + v_3r = 1$. Stated another way, the end point of a vector $\mathbf{v} = p\mathbf{a} + q\mathbf{b} + r\mathbf{c}$ lies on a plane $v_1x + v_2y + v_3z = 1$ if and only if $x = p, y = q$ and $z = r$.

For a plane to qualify as a lattice plane in S , it must pass through the end-points of three noncoplanar lattice vectors in L_D . Hence, if P is a lattice plane, then there must exist three such lattice vectors $\mathbf{p} = p_1\mathbf{a} + p_2\mathbf{b} + p_3\mathbf{c}$, $\mathbf{q} = q_1\mathbf{a} + q_2\mathbf{b} + q_3\mathbf{c}$ and $\mathbf{r} = r_1\mathbf{a} + r_2\mathbf{b} + r_3\mathbf{c}$ in L_D whose end-points lie on P where p_i , q_i and r_i are integers. As the end-points of these vectors are each on P , then the indeterminants x, y and z of the expression $v_1x + v_2y + v_3z = 1$ can be replaced successively by the coefficients of \mathbf{a} , \mathbf{b} and \mathbf{c} for each of the three vectors to yield the following three equations: $v_1p_1 + v_2p_2 + v_3p_3 = 1$, $v_1q_1 + v_2q_2 + v_3q_3 = 1$, and $v_1r_1 + v_2r_2 + v_3r_3 = 1$. Simultaneously solving these equations for v_1 , v_2 and v_3 yields three rational numbers which can be easily converted into the integers h, k and l by multiplying both sides of the equation by a common factor and clearing the resulting fractions to obtain the Miller indices of the plane P .

EXAMPLE 10: A determination of the Miller indices for a lattice plane

Suppose that the end-points of the following three noncoplanar lattice vectors $\mathbf{p} = 2\mathbf{a} - 3\mathbf{b} + \mathbf{c}$, $\mathbf{q} = -\mathbf{a} + \mathbf{b} - 2\mathbf{c}$ and $\mathbf{r} = -3\mathbf{a} + 2\mathbf{b} + 3\mathbf{c}$ in L_D lie on some lattice plane P , find the equation and its Miller indices.

SOLUTION

As observed above, the equation of a plane in S can be written as $v_1x + v_2y + v_3z = 1$ and since the end point of the three lattice vectors \mathbf{p} , \mathbf{q} and \mathbf{r} lie on a lattice plane, P , we can write the following three equations $v_1(2) + v_2(-3) + v_3(1) = 1$, $v_1(-1) + v_2(1) + v_3(-2) = 1$ and $v_1(-3) + v_2(2) + v_3(3) = 1$. Simultaneously solving these equations, we find that $v_1 = -23/12$, $v_2 = -7/4$ and $v_3 = -5/12$. Substituting these values into the equation $v_1x + v_2y + v_3z = 1$, we obtain $-23/12x - 7/4y - 5/12z = 1$. Multiplying both sides of the equation by each of the denominators of v_1 , v_2 and v_3 and clearing fractions, we obtain $-23x - 21y - 5z = 12$ as the equation of P where $h = -23$, $k = -21$ and $l = -5$ are the Miller indices of the plane.

In general, it can be shown that the equation of a lattice plane in L_D is of the form $hx + ky + lz = m$ where h, k, l and m can adopt all possible integer values, resulting in as many planes. For example, the equation $hx + ky + lz = m$ defines, for a given set of integers h, k and l , an infinite number of equally spaced, parallel planes, one for each integer value of m . It can be shown that each such plane is translationally equivalent to the plane $hx + ky + lz = 1$. The spacing between each of these planes is the well-known $d_{(hkl)}$ -spacing for the plane (hkl) . The plane $hx + ky + lz = 1$ intercepts the X -axis of the crystal at \mathbf{a}/h , the Y -axis at \mathbf{b}/k and the Z -axis at \mathbf{c}/l . The plane defined by $hx + ky + lz = m$ intercepts the X -axis of the crystal at $m\mathbf{a}/h$, the Y -axis at $m\mathbf{b}/k$ and the Z -axis at $m\mathbf{c}/l$ whereas the plane defined by the equation $hx + ky + lz = 0$ passes through the origin, $\mathbf{0}$, of the unit cell (cf. Fig. 2.3, B&G). In other words, the plane defined by the equation $hx + ky + lz = m$ is m times as far from the origin as the plane defined by the equation $hx + ky + lz = 1$. As the plane $hx + ky + lz = 1$ is translationally equivalent to each of the planes defined by the equations $hx + ky + lz = m$, it is taken as the representative plane for this infinite set of equally spaced, parallel planes in the lattice. By convention, whenever a plane with indices h, k and l is discussed, it is assumed by convention to be the plane defined by the equation $hx + ky + lz = 1$, located at a distance of $d_{(hkl)}$ from the origin of the unit cell. For another but similar development of the equation of a lattice plane, Miller indices and a derivation of an expression for the $d_{(hkl)}$ -spacing see B&G (p. 42-47 and Appendix 5).

PROBLEM 8: Determine the equation of the lattice plane in L_D that passes through the end-points of the vectors $\mathbf{p} = 3\mathbf{a}$, $\mathbf{q} = -\mathbf{b}$ and $\mathbf{r} = 2\mathbf{c}$.

SOLUTION

In this example, we want to find the equation of a plane that passes through the end-

points of the three vectors \mathbf{p} , \mathbf{q} and \mathbf{r} that lie along the X -, Y - and Z -coordination axes, respectively. With the information given, the following three equations can be written : $3v_1 = 1$, $-1v_2 = 1$ and $2v_3 = 1$. It follows that $v_1 = 1/3$, $v_2 = -1$ and $v_3 = 1/2$. Replacing v_1 , v_2 and v_3 in $v_1x + v_2y + v_3z = 1$ by $1/3$, -1 and $1/2$, respectively, the equation $1/3x - y + 1/2z = 1$ is obtained. Multiplying both sides of the equation by 6 and clearing fractions, $2x - 6y + 3z = 6$ results as the equation of the plane that passes through the end-points of the lattice vectors $3\mathbf{a}$, $-1\mathbf{b}$ and $2\mathbf{c}$. The Miller indices of this plane are $(2\ -6\ 3)$.

PROBLEM 9: Determine the equation and the Miller indices of a lattice plane that passes through the end-points of the following three noncoplanar lattice vectors $\mathbf{v}_1 = 1\mathbf{a} + 2\mathbf{b} + 5\mathbf{c}$, $\mathbf{v}_2 = 2\mathbf{a} - 1\mathbf{b} - 6\mathbf{c}$ and $\mathbf{v}_3 = -1\mathbf{a} - 1\mathbf{b} + 0\mathbf{c}$.

SOLUTION

$$(2, -3\ 1) \text{ and } 2x - 3y + z = 1$$

CONCLUDING REMARKS

The selection of a set of basis vectors in an X-ray diffraction study is an important first step in the study of the geometrical properties of a mineral. Once this is done, the metrical matrix is easily computed and the geometry of the mineral is completely characterized. With the matrix and a knowledge of the rules of matrix multiplication and matrix inversion, a variety of relatively difficult crystallographic problems can be solved with surprisingly little effort, particularly when the computations are completed with the program MATOP. Also, with a simple rule for determining the equation of a plane, the Miller indices of a lattice (crystal) plane can be determined in a straightforward way. With the use of the rule, one avoids using Weiss parameters which have not only outlived their usefulness but should be purged from the mineralogical literature.

ACKNOWLEDGEMENTS

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FROM 2D TO 3D: I. ESCHER DRAWINGS

CRYSTALLOGRAPHY, CRYSTAL CHEMISTRY, AND CRYSTAL “DEFECTS”

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PREFACE TO INSTRUCTOR

This set of exercises illustrates **A.** plane and space groups and **B.** crystal chemistry and “defects” in crystals. The problems are designed to present the material as puzzles that are visually attractive and intellectually challenging. Parts **A** and **B** can be covered independently of one another. Part **B** flows into the following problem set, “From 2D to 3D: II. HRTEM and AFM images” (Buseck, this volume), which provides examples of real crystals through high-resolution images from both transmission electron microscopy (HRTEM) and atomic-force microscopy (AFM). The exercises can be used either as take-home problem sets or as laboratory exercises.

Several exercises use drawings by M.C. Escher and one by I. Schaschl to take the students to another level of sophistication from that in many texts and to see whether they can draw mineralogical analogies from these drawings (a strange thought, considering these are just weird, artistic fantasies of animals and more abstract motifs). We also look at **deviations** from ideality as they occur in minerals. These are examples of the wide range of fascinating features that are encountered in real (as opposed to idealized) minerals.

There is too much material to be covered in a single laboratory session. However, it is possible to select from among the problems, choosing those that are most relevant to the particular topic being covered. The two problems of topic **A**, “Escher drawings as 3-D projections: analogies to real minerals,” take the most time. They can be skipped if crystal chemistry and mineral defects are the topics of greatest interest.

Problems 3 to 6, grouped under topic **B** “Order/disorder relations,” provide examples of features found in real minerals (superstructures, substitutions and structural “defects,” and modulated and incommensurate structures). Only some of these complexities are covered in the typical introductory mineralogy course. Comments I received at the Workshop were encouraging. Some participants, themselves mineralogy instructors, commented that some of these mineralogical complexities made sense to them for the first time in the process of doing these problems.

Students should have prior familiarity with basic symmetry elements, unit cells (in two dimensions, even if not in three), and have been exposed to the concept of plane groups. These topics are covered in most mineralogy textbooks, and students may wish to consult those texts (a worthwhile goal in itself) in the course of doing these problems. The insights provided in these exercises are reinforced by comparison to the exercises in the following problem set, “From 2D to 3D: II. HRTEM and AFM images,” in which TEM and AFM images of real minerals are considered.

Materials: Escher drawings # 42, 55, 70, 78, and “*Birds in Space*,” plus “*Iselberg*” by I. Schaschl (Vienna Museum); transparent overlays (plastic overhead sheets do well); colored markers (I like Staedtler Lumocolors); a reference copy of the *International Tables for Crystallography* (ref. given below). I found it effective to use sequential overlays in demonstrations to explain the steps in figuring out the relationships in problems #1 and 2.

- b) Show where these new symmetry elements occur by marking them onto a transparent overlay and by giving their fractional xy coordinates (e.g., 0, 0; $1/2$, $1/2$; 0, $1/3$, etc.).
- c) What is the relevant Bravais lattice of this projected 3D pattern?
We now have a 3D array that can be described as a **space group** rather than one of the 2D **plane groups**. Such a 3D array might also have new symmetry elements that are oriented horizontally, either within the plane of the pattern or above it, and they are required to recognize exactly which space group is represented. With the experience at hand, it would be difficult to identify each of these new symmetry elements. However, it is possible to use the available information to identify *possible* space groups.
- d) Using the *International Tables for Crystallography*, name and give the space group number (marked at the top of the page in the *IT*) of one or more space groups that are compatible with this symmetry? For purposes of this problem, it is acceptable to hypothesize the presence (or absence) of inversion centers and horizontal axes of rotation, but no other symmetry elements that are not evident upon inspection.
Hint: note that in the *IT* the space groups are organized by crystallographic system: # 1 and 2 - **triclinic**; 3 to 15 - **monoclinic**; 16 to 74 - **orthorhombic**; 75 to 142 - **tetragonal**; 143 to 194 - **hexagonal**; 195 - 230 - **isometric**. Within each crystal system they are arranged in order of increasing symmetry.
- e) Explain your reasoning in arriving at the space groups you selected.
[It may be useful to generate cross sections that show the types of drawings at each level, e.g., red butterflies with blue dots, etc. Only a stacking of color pairs is needed to show the sequence.]
- f) Note that these groups correspond to some important minerals. Name a common mineral that corresponds to a space group given above. [It may be necessary to hypothesize inversion centers or horizontal axes, as specified in d).]
- g) If mirrors or glides were added, which additional common minerals would be included?
- h) Two-fold axes occur in the “color-blind” pattern but not in the colored 2-D pattern. What is their status in the 3-D pattern?

B. ESCHER & SCHASCHL DRAWINGS: ORDER/DISORDER RELATIONS

SUPERSTRUCTURES

3. Escher pattern #78 (“Unicorn”) contains red, yellow, and green unicorns that are identical except in color.
- a) Ignoring the color differences, determine the symmetry, mark a unit cell, and determine the plane group
- b) Now repeat a) considering the color differences.
- c) Does the colored or “color-blind” pattern have the larger unit cell? By what factor?
- d) Has the plane group changed? If so, to what?
- e) The relation between these two cells is that one could be called a **supercell** and the other is then the **subcell**. Structures formed in this way are called **superstructures**. Which structure (colored or “color-blind”) defines the **subcell**, which the **supercell**, and which is the **superstructure**?
- f) Assume that parts of one pattern represent the atoms or atom groups in a mineral structure that formed at high temperatures and then transformed during cooling to a structure that is stable at low temperature. Many common oxide, sulfide, and silicate minerals display such transformations. Which pattern would be the more appropriate one for low temperatures? Explain your answer.

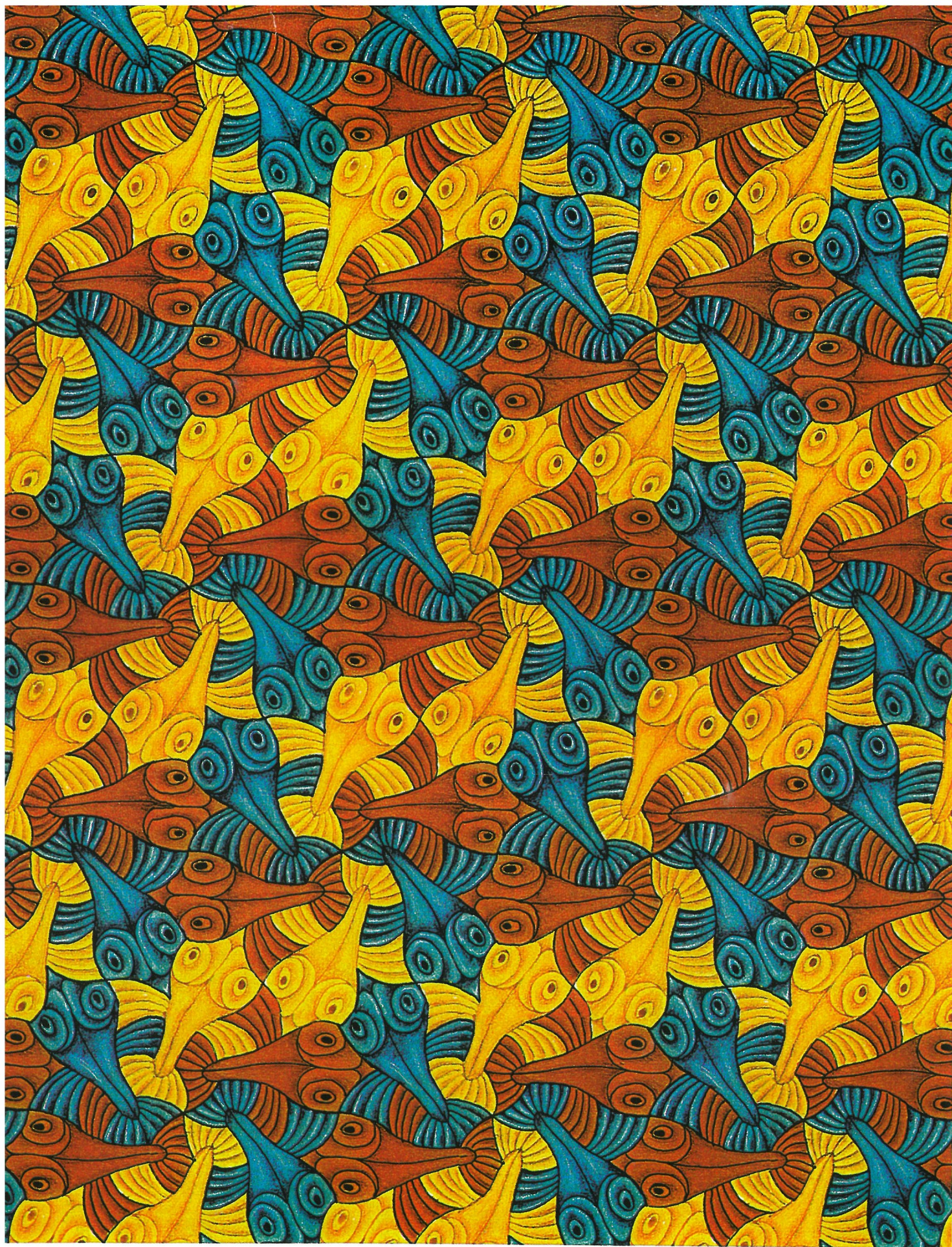


Figure 1. Escher Pattern #55 (*Fish*), reproduced with permission of Cordon Art.

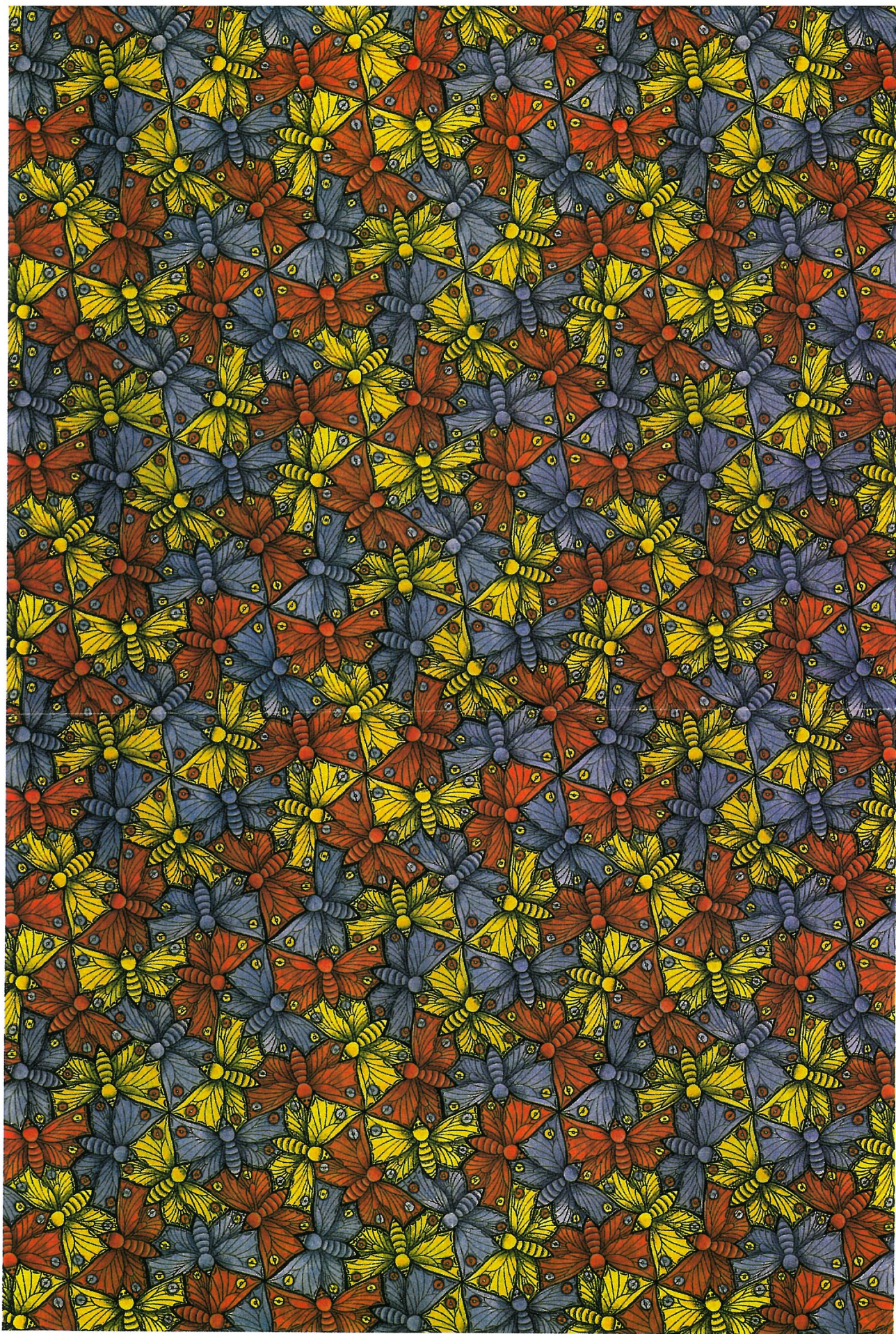


Figure 2. Escher Pattern #70 (*Butterfly*), reproduced with permission of Cordon Art.

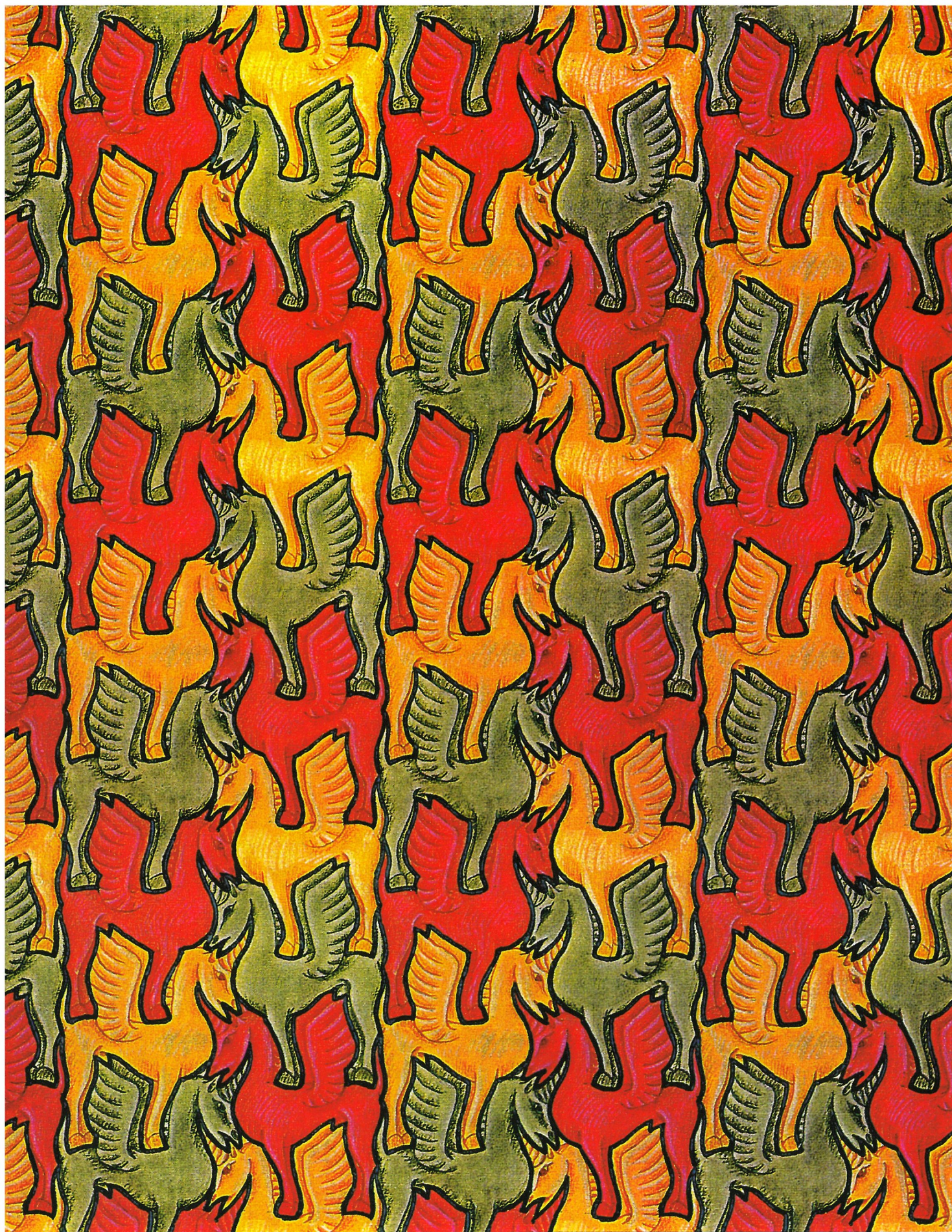


Figure 3. Escher Pattern #78 (*Unicorn*), reproduced with permission of Cordon Art.

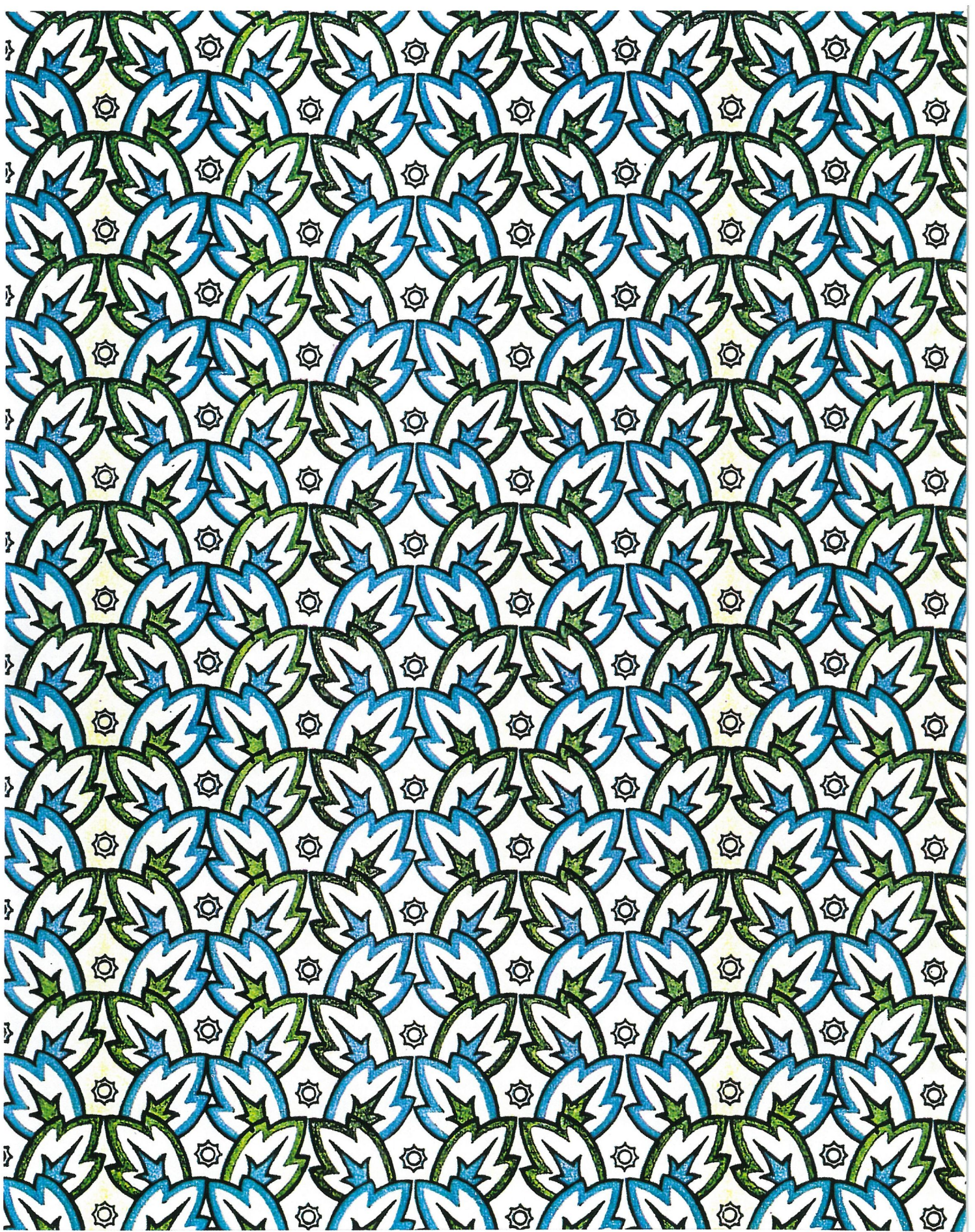


Figure 4. *Iselberg* by Irene Schaschl, reproduced with permission of MAK.

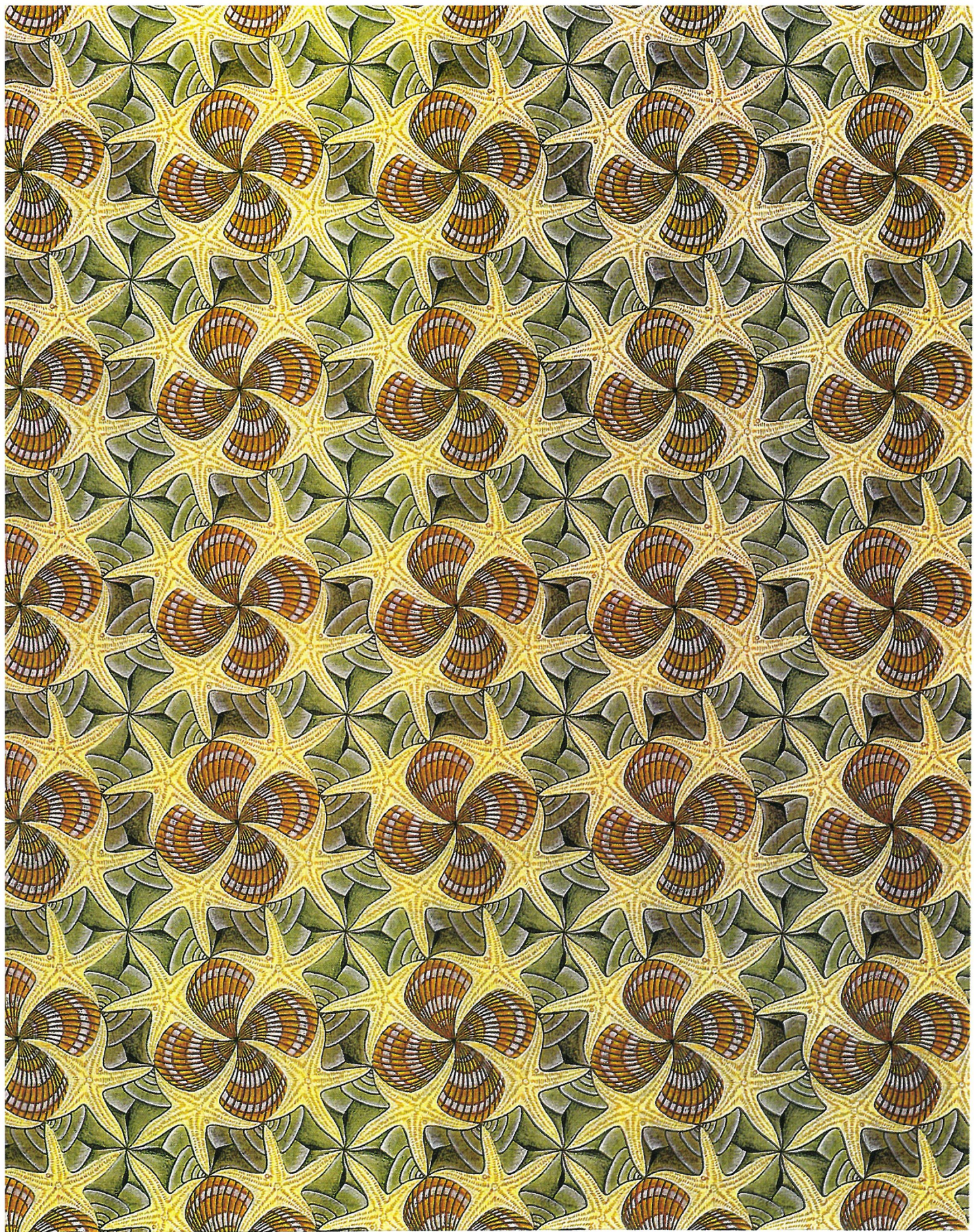


Figure 5. Escher Pattern #43 (*Shells and Starfish*),
reproduced with permission of Cordon Art.

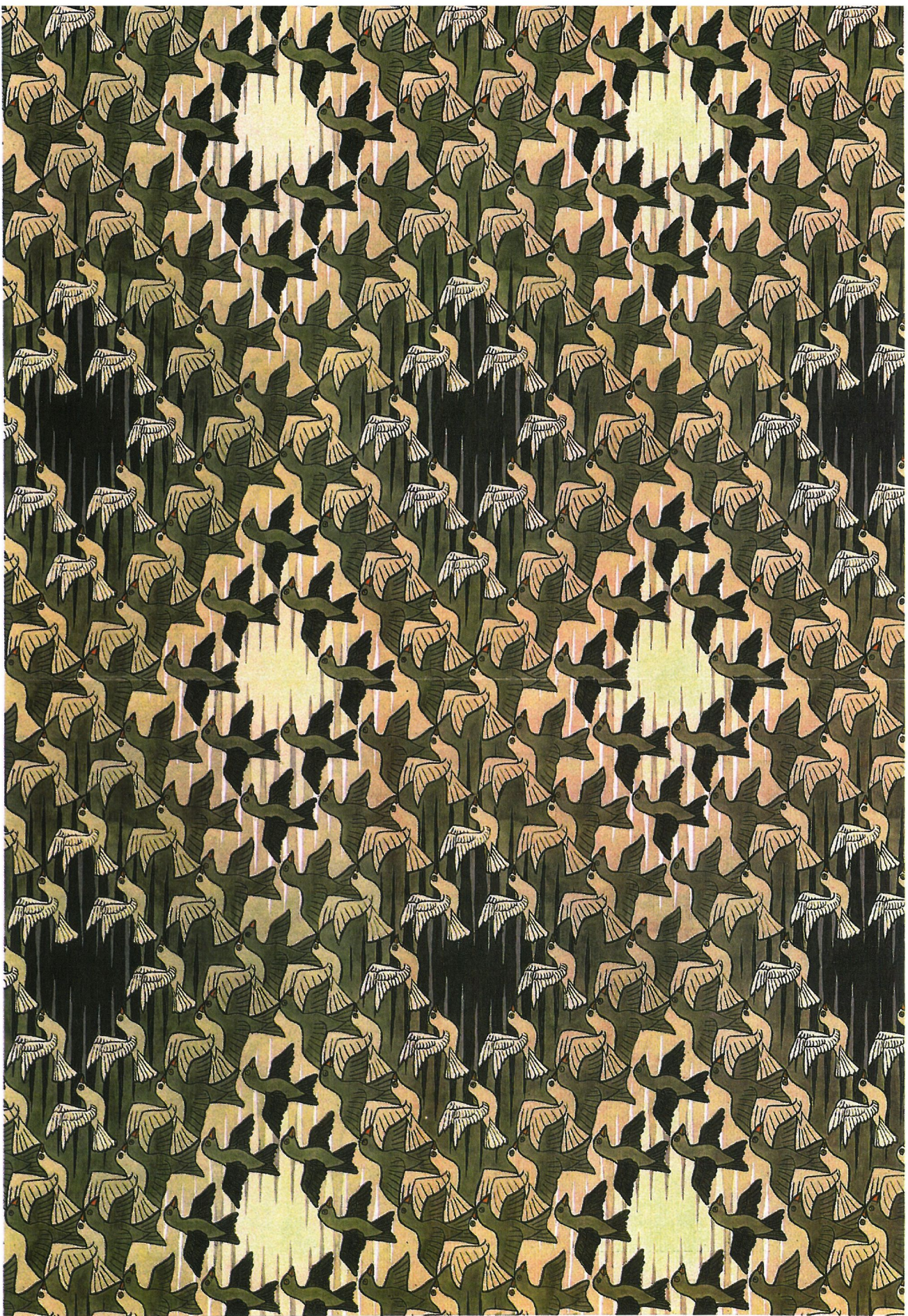


Figure 6. *Birds in Space* by M.C. Escher, reproduced with permission of Cordon Art.

(A mineralogical analog might be that of a mineral such as chalcocite, in which the Cu and Fe atoms are randomly distributed onto the metal sites at high temperatures and then ordered at low temperatures to produce a new cell having different dimensions. [In the case of pattern #78, the analogy would be with a mineral having three cations (e.g., Cu, Fe, Zn; Fe, Mg, Mn; etc.) in solid solution at high temperatures which then order upon cooling.]

4. This pattern ("Iselberg" by Irene Schaschl) provides another example of a feature having a longer periodicity than what by first (and second) glance appears to be the basic repeat unit, although it is more subtle to see. Note that the tips of the leaves touch in some vertical rows and do not in others.
- a) Draw unit cells:
- ignoring the above subtlety, i.e., assume the touching leaves are just a mistake by the artist, and
 - considering that there is a real difference between the touching and non-touching leaves.
- b) What is the dimensional (metric) relationship between cells for assumptions (i) and (ii)?
- c) The following patterns contain repeating units that also can be considered on two scales, easiest seen by noting the periodicity first of the squares (\square representing, for example, anions) and then of the squares plus intervening symbols ($\blacktriangle\blacklozenge$) representing cations. Assume that none of the ordered repeat units for the following patterns extend across more than half of the page (so that at least two repeat units are shown). Indicate the width of the unit cell and give its pattern. Recall that a disordered cell can be considered to have "average" site occupancies.



repeat unit:



repeat unit:



repeat unit:



repeat unit:



repeat unit:

MODULATED AND INCOMMENSURATE STRUCTURES

6. Escher pattern of **Birds in space** is truly fascinating and reflects a type of disorder that is becoming increasingly apparent as our methods for studying minerals (and other crystals) become more sophisticated. It shows the two types of birds changing into one another as the pattern is traversed. The large black and white areas can be seen as isolated point defects (perhaps more realistically, clustered point defects), and they are periodically arrayed.

The result is the analog of a superstructure. Supercells have dimensions that are multiples of the subcell.

In some minerals, the supercells are integral multiples (e.g., $n = 2, 3, 4, \dots$) of the subcell. They are then called *commensurate*. Sulfides such as chalcopyrite, silicates such as long-period polytypes of mica and chlorite, and oxides such as hollandites form commensurate superstructures.

In other superstructures the supercells are not integral multiples of the subcell. They are then called *incommensurate*. Many sulfide and sulfosalts (e.g., pyrrhotite, franckeite), silicates (e.g., plagioclase, antigorite serpentine), and oxides (e.g., intermediate tridymite) form incommensurate superstructures.

Incommensurate superstructures have also been called “vernier” materials because their units mesh like a vernier on surveying or measuring instruments (e.g., transit, theodolite, alidade).

Superstructures such as are mentioned above are becoming of increasing mineralogical and industrial interest. Their utility for industrial purposes is that it is possible to make “designer” materials whose properties depend on subtle variations in structure such as is possible when there are slight dimensional or motif mismatches.

Back to the Escher drawing, it can be difficult to define a unique subcell.

The most unambiguous periodicity in this pattern is the large repeat defined by the large black (and white) “holes” or “defects” in the pattern. We shall call the cell defined by these “holes” a supercell and place its origin in the center of the “hole.”

There is also an underlying periodicity of intermediate spacing (and so described as a subcell), although it is more difficult to recognize and define because of its inexactness. Viewing the pattern from a distance while squinting helps make the subcell periodicity evident.

- On an overlay mark a subcell with a horizontal cell edge that is defined by the white birds. What is the relation of the width of the subcell to the supercell in terms of numbers of birds – if the origin of the supercell is placed (i) on the center of the black holes? (ii) on the center of the white holes?
- As a further complexity, consider a line in a southeast direction from the black to the white holes. How many white birds do you count?
- Now count in a northeast direction from the black to the white holes. What number of white birds do you come up with? This difficulty in defining the repeating unit is characteristic of incommensurate structures where there is not a perfect dimensional match between the component parts.
- Draw a unit cell of the substructure. Note that you will have to assume a uniformity that does not really exist in detail, only in shape. Indicate where you chose the origin and how you decided on that choice.
- Draw a unit cell of the superstructure. What are its dimensions in terms of subcell repeats?

Answers for "FROM 2D TO 3D: I. ESCHER DRAWINGS"

1. **PART I** – a) yes – 2-fold rotation axes at the corners of the unit cell and midway along each cell edge and in the center of the cell; c) p2; d) 2's at tails --> 6's; 2's at eyes --> no change; 3's appear next to other eyes, i.e., along the long body diagonal at $1/3$, $2/3$ and $2/3$, $1/3$; e) no, no; f) p6. **PART II** – a) 3; b) the cell corners are located at the intersection of the 6_2 or 6_4 screw axes with the pattern; c) [1] 6, yes, 3, $2p/6$, 6_2 or 6_4 screw axes; [2] 2, no, 1, $2p/2$, 2-folds; [3] 3, yes, 3, $2p/3$, 3_1 or 3_2 screw axes; [4] none; d) [1] $P6_2$ - # 171 & $P6_4$ - # 172 or $P6_22$ - # 180 & $P6_422$ - # 181; [2] they are enantiomorphic pairs.

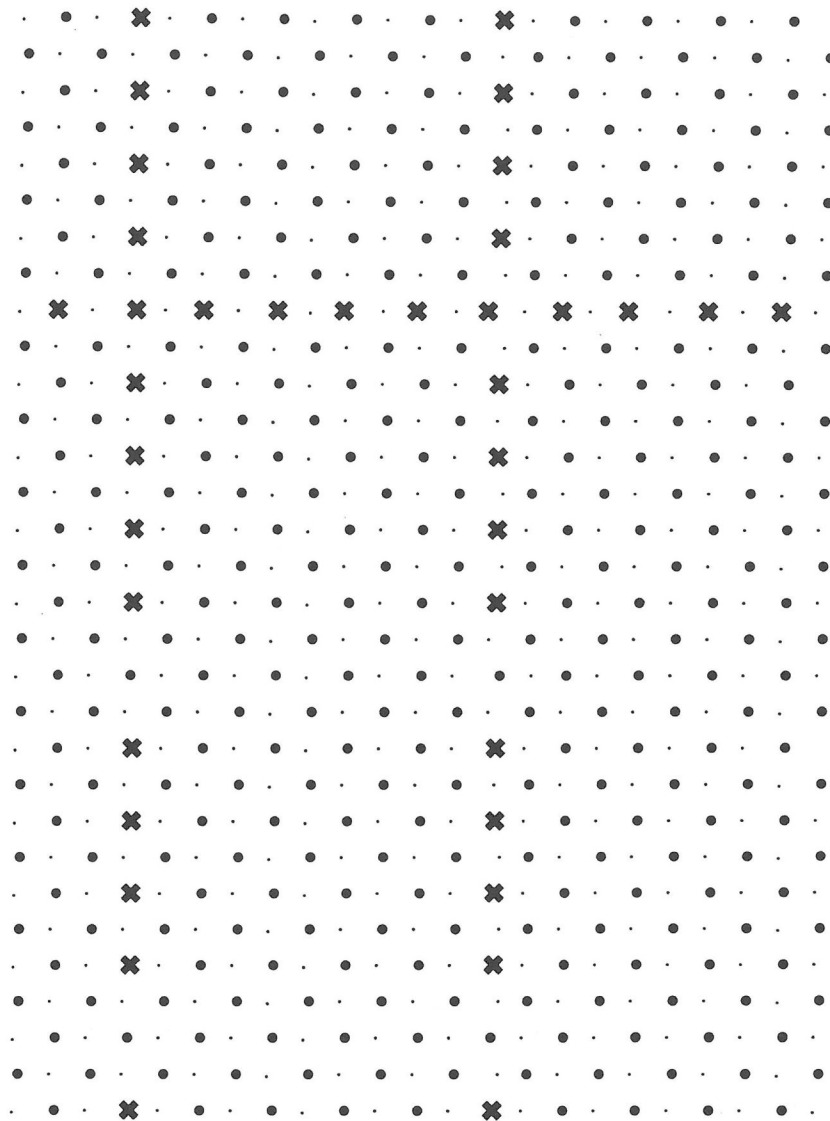
2. **PART I** – a) yes – 3-fold rotation axes at the corners of the unit cell and along the long body diagonal at $1/3$, $2/3$ and $2/3$, $1/3$; c) no; d) three for the 3's, i. e., there are three distinct color combinations around the 3 folds; e) p3; f) 3's --> 6's; new 2's between the 6's; new 3's along the long body diagonal at $1/2$, $1/2$; $1/3$, $2/3$; and $2/3$, $1/3$; g) yes; yes; it becomes rhomb shaped with its long body diagonal along the cell edge of the "colored" unit cell; h) the p3 cell with color is 3 times larger than the (colorblind) p6 cell i) p6.

PART II – a) 3-fold screw axes; b) at $1/3$ and $2/3$ along each cell edge, i.e., at $1/3$, 0; $2/3$, 0; 0, $1/3$; 0, $2/3$ and at $1/3$, $1/3$; $2/3$, $2/3$ within the cell; c) R; d) $R3$, #146, or $R3$, #148, if inversion centers are present or $R32$, #155, if horizontal 2-folds are present; e) the R lattice and 3-fold screws limit the answer to the above; $R3m$, #160; $R3c$, #161; $R3m$, #166; and $R3c$, #167 are not possibilities because no mirrors or glides are evident; f) $R3$ – dolomite, ilmenite; for dolomite: At 3s at cell corners (lattice nodes): red butterflies with blue spots represent oxygens along the top of Ca octahedra and yellow butterflies with blue spots represent oxygens along the bottoms of Ca octahedra. At 3s along the long body diagonal: $2/3$, $1/3$ – blue butterflies with red spots represent oxygens along the top of Ca octahedra, and $1/3$, $2/3$ – blue butterflies with yellow spots represent oxygens along the bottoms of Ca octahedra g) $R3m$ – tourmaline; $R3c$ – hematite, corundum, calcite; h) they are absent – the butterflies at the positions of these presumptive 2-folds are at levels separated by $1/3$ and there is no 2-fold that has that property.

3. a) there are vertical glide planes; the position of the unit cell is defined by the glide planes; pg; b) the same as a) *except that* the unit cell is three times as high; c) colored; x3; if the color differences are ignored, then a unit cell $1/3$ the size of the "color-inclusive" cell is defined; d) it is still pg; e) colored – supercell & superstructure; "color-blind" – subcell; f) the larger cell is the result of ordering of atoms (here represented by motifs) upon cooling. Such formation of superstructures at low temperatures is common among all minerals, and especially among ore minerals such as sulfides.

4. a) note the every third pair of leaves along horizontal rows is touching, and there are narrow gaps between the tips of intervening leaves; b) cell ii has triple the area (triple the length) of cell i; c) repeat units: $\blacktriangle \blacklozenge \square$; $\blacktriangle \blacklozenge \square \blacktriangle \square$; *disordered*; $\blacktriangle \blacklozenge \square$ or $\blacklozenge \blacktriangle \square$; $\blacktriangle \blacklozenge \square \blacktriangle \square \blacktriangle \square$; $\blacktriangle \blacklozenge \square \blacktriangle \blacklozenge \square \blacktriangle \square$; d) $\blacktriangle \blacktriangle \square \blacklozenge \blacklozenge \square \blacklozenge \blacklozenge \square \blacktriangle \blacktriangle \square \blacklozenge \blacklozenge \square \blacklozenge \blacklozenge \square \blacktriangle \blacktriangle$; e) if $\blacklozenge \square \blacklozenge$ are used to approximate a calcite layer while $\blacktriangle \square \blacklozenge$ approximates a dolomite layer, then we have repeating layers of dolomite, calcite, calcite, ..., i.e., a Mg-rich calcite or a calcic "dolomite".

5. a)



b) the pattern is not perfectly periodic because some brown snails have reversed orientations; however, the positions of the components of the drawing are perfectly periodic; [1] K^+ & Cs^+ : probably not since size differences would produce structural distortions; Ti^{+4} & Fe^{+2} : no – charge differences; would probably structural distortions; Fe^{+2} & Fe^{+3} : no – size & charge differences; would produce structural distortions; Fe^{+2} & Mg^{+2} : OK; Ca^{+2} & Mg^{+2} : probably not – size differences; would produce structural distortions; Si^{+4} & Al^{+3} : perhaps; they do substitute for one another in tetrahedral sites; Cu^{+2} & Zn^{+2} : OK; [2] the lattice is perfectly periodic, and most parts of the motifs are periodic. It is only the brown snails that disrupt the perfect periodicity. Technically, there is local order and overall disorder with respect to the brown snails; [3] TEMy, but even then, only if the brown snails generate sufficient contrast, as might occur if they were heavy metals. Mineralogical examples include vacancies in pyrrhotite or clusters in digenite

6. a) the supercell is (i) 4x that of the subcell when the supercell origin is placed on the center of the black holes, and (ii) 4x when on the white holes; b) ~4; c) ~4; d) there is no symmetry, so there is freedom in where to choose the origin; the dimensions are those from one bird to another either horizontally or along the diagonals; e) 4 x 5.

FROM 2D to 3D: II. TEM and AFM IMAGES

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PREFACE TO INSTRUCTOR

The problems in the accompanying exercises, "From 2D to 3D: I. Escher drawings" (Buseck, this volume), deal with abstractions that can be related to minerals through geometrical features they have in common. However, we are ultimately interested in real minerals, their symmetries and complexities. High-resolution transmission electron microscopy (HRTEM) provides 2-D projections of mineral structures at almost the atomic scale, and atomic force microscopy (AFM) provides 3-D information about the surfaces of minerals.

Although obtained by using completely different instruments that are based on totally different principles, the two approaches provide complementary information. Both can yield information about defects in minerals. They thus leap the broad gap between the idealized structure models that we commonly use to introduce minerals and the actuality of minerals, their faults and other complexities.

The mineral examples in this problem set include representative of several silicates structure types (cordierite, crocidolite, alkali feldspar), sulfides (bornite, digenite, pyrrhotite), a sulfosalt (francite), and a carbonate (dolomite/ankerite). Interpretation of the images is less clear-cut than of the idealized drawings. In some cases the results can be ambiguous, but they provide scope for fruitful discussions among class members. Parts of the section on alkali feldspars require a basic familiarity with and knowledge of the reciprocal lattice and interpreting simple diffraction patterns.

In a few cases, references are given to the published papers from which the images are taken (*American Mineralogist*, *Science*, *Physics and Chemistry of Minerals*). These can be used to draw students into the professional literature, although even then it will not always be possible to arrive at unambiguous answers. These problems should be thought provoking and yet manageable at several levels of complexity. Good luck!

HRTEM IMAGES, PLANE GROUPS, AND SYMMETRY

1. **Plane groups and symmetry: cordierite/"problemite"** Figure 1 (which also appears as Figure 3.19 in Klein and Hurlbut *21st ed.*, p.128) is a high-resolution photograph of a crystal of cordierite taken with the transmission electron microscope. Assume that the authors misidentified it and that this new mineral, we'll call it "problemite," should have $a = 16.8\text{\AA}$ (instead of 17.1\AA). It can now be assigned to a crystal system having a higher symmetry than the one of cordierite.
 - a) For the "problemite" locate rotation axes with "folds" greater than two that are oriented perpendicular to the page. Mark these on an overlay
 - b) Mark a unit cell for the "problemite." (Hint: is it rectangular?)
 - c) Does it have the same number of lattice nodes as the cordierite cell? If not, how do they differ?
 - d) What is the crystallographic system of problemite? Explain your answer.

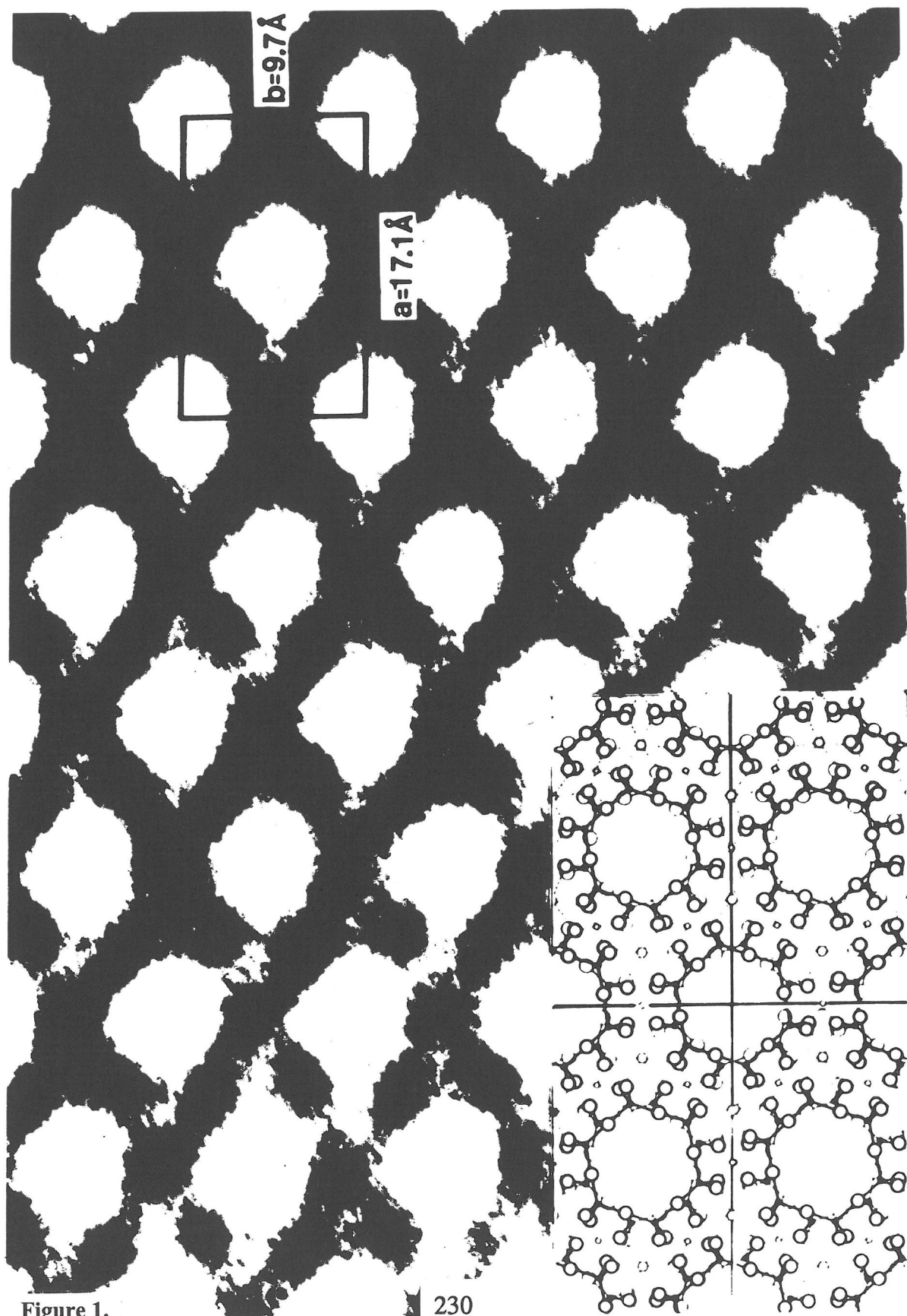


Figure 1.

2. HRTEM images and the Escher and Schaschl drawings

The following consist of HRTEM images of real minerals that display some of the features that were illustrated through the use of the Escher and Schaschl drawings. The challenge is to try and correlate the TEM images of real minerals with the idealizations represented by the art drawings. The answers are not always obvious, and the interpretations are open to question, which can provide scope for discussion.

- a) **Bornite and digenite.** Superstructures can form through the ordering of vacancies along the join connecting digenite ($\sim\text{Cu}_{7.2}\text{S}_4$) and bornite (Cu_5FeS_4), two minerals that are abundant in Cu ore deposits. The end-member species contain ordered vacancies, and these vacancies diffuse and cluster in minerals having intermediate compositions (Pierce and Buseck, *Am. Min.* **63**, 1–16, 1978). Figures 2a₁ and a₂ (taken by L. Pierce) show periodically arranged light and dark regions in bornite and digenite, respectively.
- [1] Mark a unit cell on each of the images (since they are projections of the crystal structures, assume they are of 2-dimensional crystals). If you encounter difficulties, explain why.
 - [2] Indicate the symmetry elements consistent with a plane (reflection lines and rotation axes perpendicular to the plane).
 - [3] To which Escher or Schaschl drawing(s) in the previous problem set, "From 2D to 3D: I. Escher drawings" (Buseck, this volume), do they best correspond? Explain your answer.
- b) **Franckeite.** The HRTEM image of franckeite ($\sim\text{FeSn}_3\text{Pb}_5\text{Sb}_2\text{S}_{14}$; Figure 2b), a mineral found in hydrothermal Ag-Sn ore deposits, shows a wavy structure (modulation) that results from the dimensional misfit between interleaved PbS and SnS₂ sheets. (Wang, Buseck, and Liu, 1995, *Am. Min.* **80**, 1174-78; photo by T. Sharp).
- [1] Mark a unit cell on the image. Indicate the symmetry elements consistent with a plane (rotation axes, reflection lines). If you encounter difficulties, explain why.
 - [2] Which is the PbS layer? Explain your answer.
 - [3] Which of the Escher or Schaschl drawings does it best match? Explain why.
- c) **Pyrrhotite.** The dark-field HRTEM image of Figure 2c is of Fe_{1-x}S , pyrrhotite (Pierce and Buseck, *Science* **186**, 1209–1212, 1974; a similar photo is reproduced on p. 236 of Klein and Hurlbut, 21st ed.). This is an example of a "defect structure," and it displays "omission" solid solution. The white spots represent columns of iron atoms viewed end-on; their intensity presumably reflects their approximate concentration, i.e., occupancy in those positions. The "missing" irons give rise to the darker spots in the image (and to the "x" in the formula).
- [1] Mark a unit cell on the image. Indicate the symmetry elements consistent with a plane (rotation axes, reflection lines). If you encounter difficulties, explain why.
 - [2] What is the relation between an Fe-deficient cell and a subcell that does not indicate an Fe deficiency? Explain your answer.
 - [3] Which of the Escher or Schaschl drawings does it best match? Explain why.
- d) **Dolomite/ankerite.** The HRTEM image (Figure 2d) of ankerite (Ca, Fe, Mg carbonate) with a superimposed simulated image of dolomite (Ca, Mg carbonate; region D) and γ -dolomite (Ca-rich dolomite; region C). Assume that the white spots represent columns of cations viewed end-on. (Because of their relatively low electron density, i.e., light atoms, the CO_3 anions are not visible). γ -dolomite contains layers of Ca that alternate with layers of Ca + Mg. The excellent matches between experimental and simulated

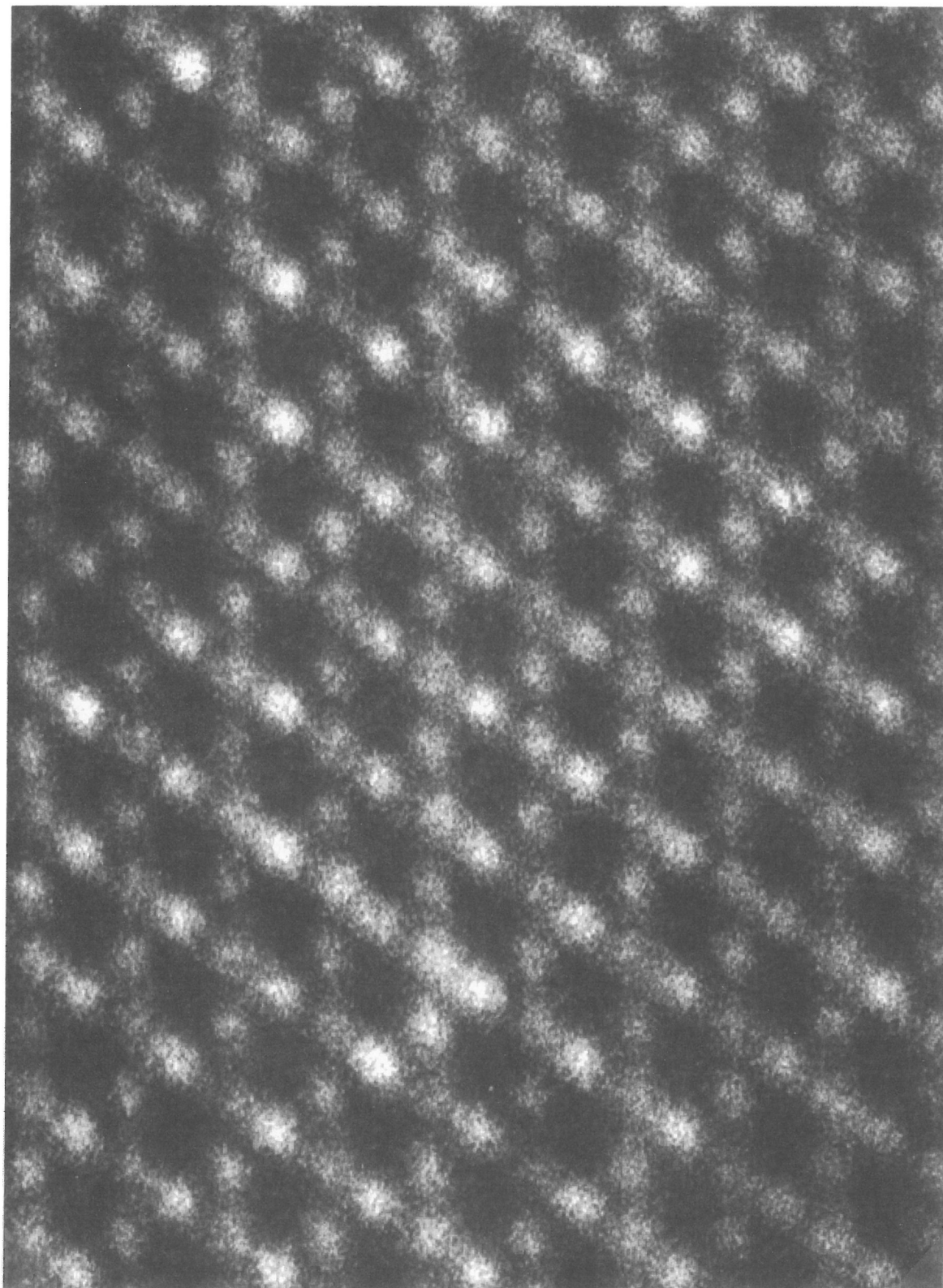


Figure 2a₁. HRTEM image of bornite.

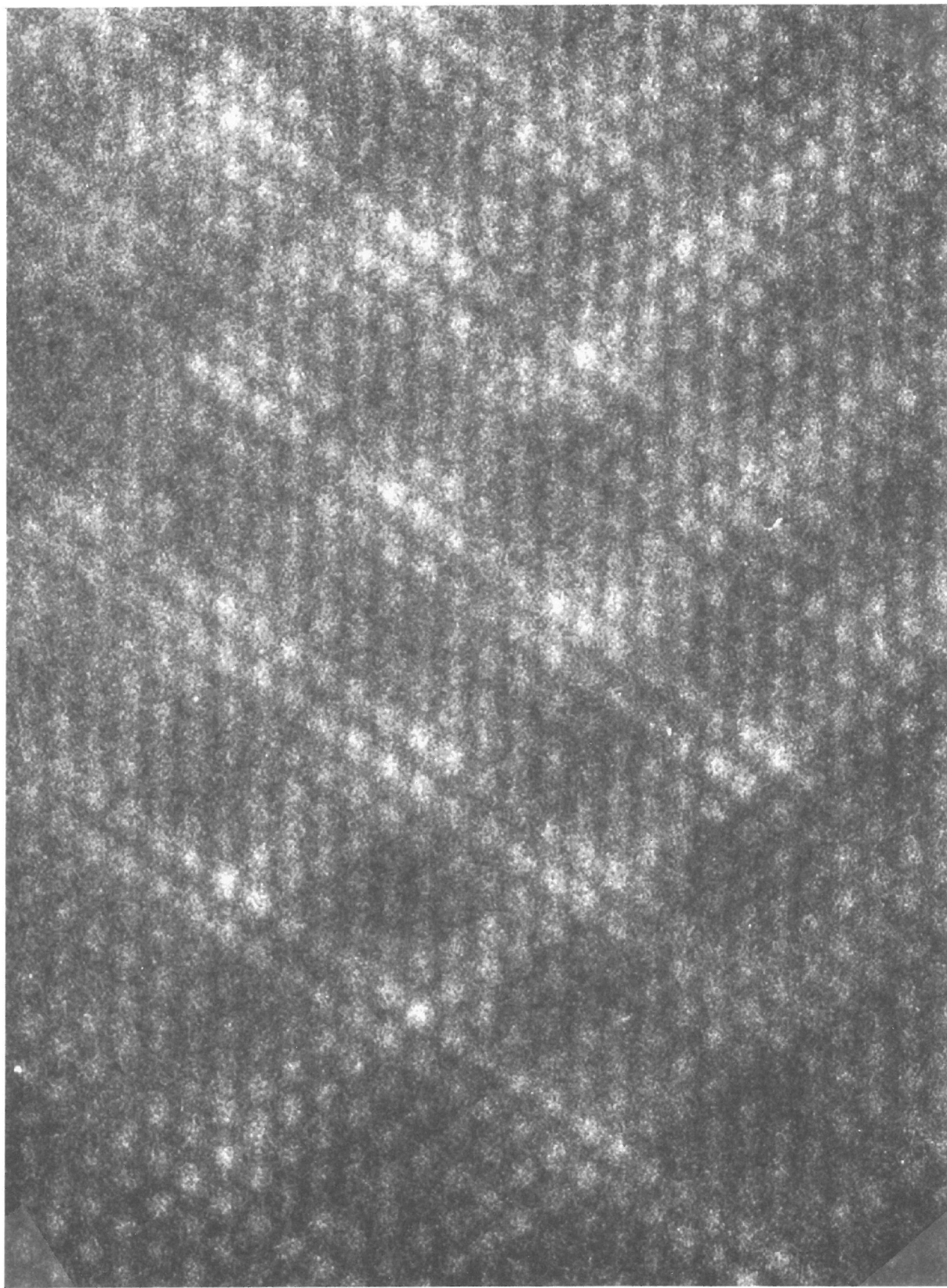


Figure 2a₂. HRTEM image of digenite.

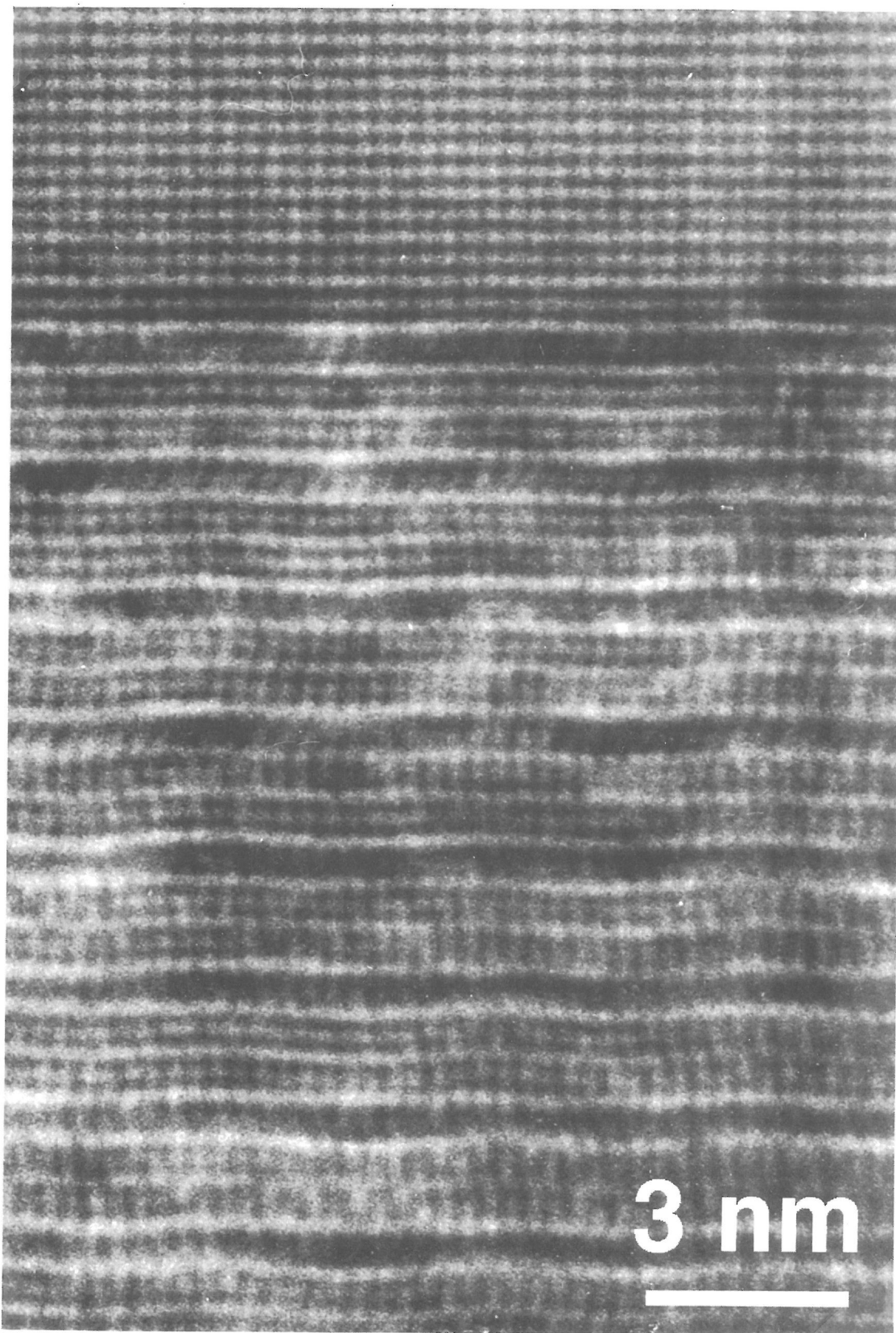


Figure 2b. HRTEM image of franckeite.

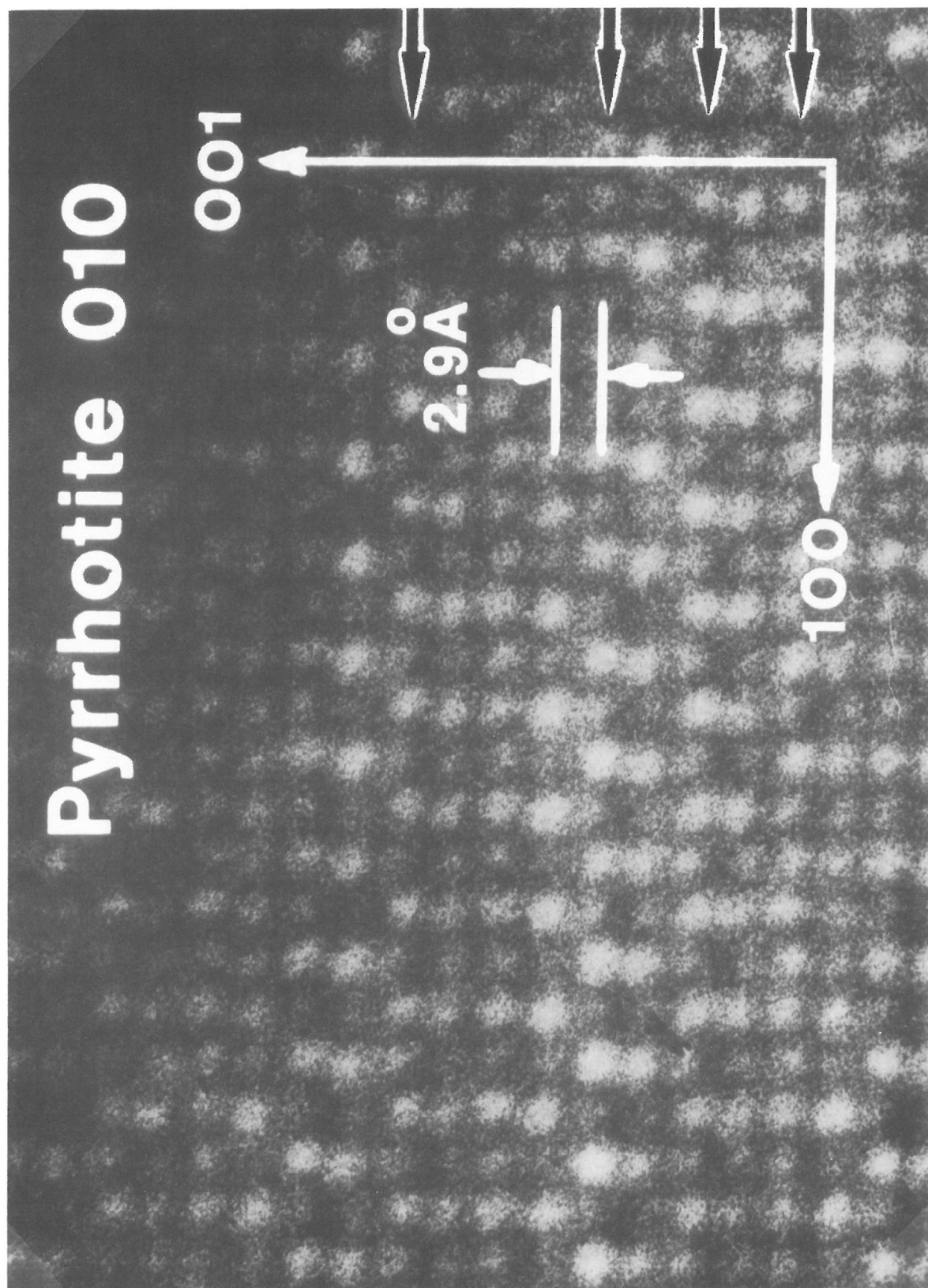


Figure 2c. HRTEM image of pyrrhotite.

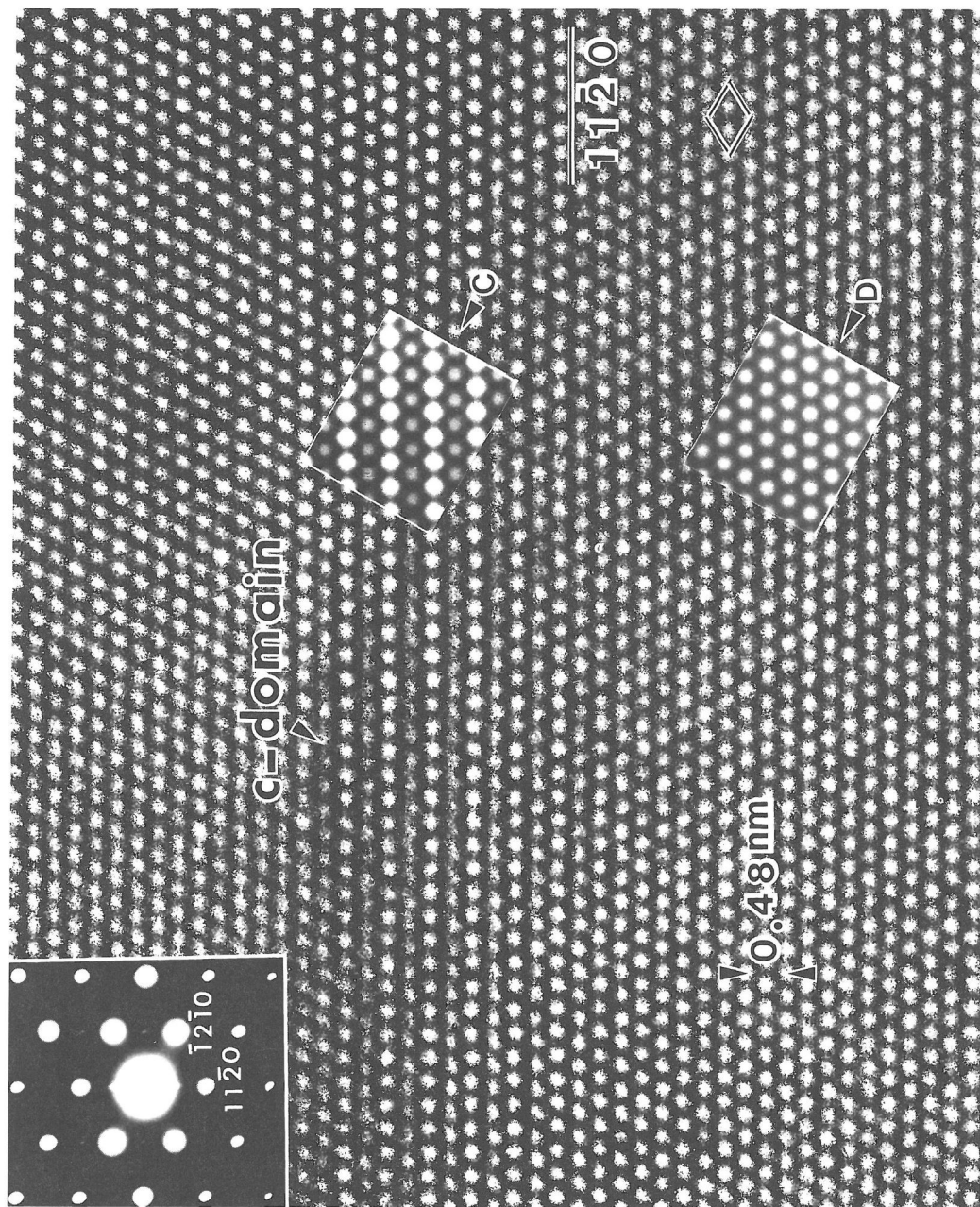


Figure 2d. HRTEM image of ankerite with a superimposed simulated image of dolomite.

images show the dolomite approximations are reasonable. (Photo from Wenk et al., *Phys. Chem. Min.* **17**, 527-529, 1991).

- [1] For region C, indicate on an overlay which layers represent mainly Ca atoms and which Ca + Mg atoms. Explain your answer.
- [2] Which of the Escher or Schaschl drawings does region C best match? Explain why.

3. HRTEM IMAGES AND FIBROUS CROCIDOLITE

- a) **Crocidolite: fibrous amphibole asbestos.** The HRTEM image in Figure 3a shows fibrous crocidolite end-on (from Fig. 3 in Ahn and Buseck, *Am. Mineral.* **76**, 1467–1478, 1991). Note the large crystal that occupies the greatest part of this image and the medium-sized grain in the lower-right area.
 - [1] What is the crystallographic and geometric relation between these two grains?
 - [2] What evidence is there that these two grains did or did not form independently of one another or that one formed from the other?
 - [3] What implications might this observation have regarding the origin of fibrosity in crocidolite asbestos?
- b) Figure 3b is another HRTEM image that shows crocidolite fibers end-on (from Fig. 13 in Ahn and Buseck, *Am. Mineral.* **76**, 1467–1478, 1991; also in Klein and Hurlbut, 21st ed., p. 165). The orientations of these grains can be determined from the defects – called “zipper” or “chain-width errors” – that are oriented perpendicular to [010]. They are chains that are wider than the double-chains of the idealized host crocidolite amphibole.
 - [1] Using the zippers, measure the angular mismatch between adjacent grains
 - [2] Note the material along the grain boundaries. From your knowledge of mineralogy and the structure of amphiboles, what might this material be?
 - [3] There are many additional questions that could be posed about the “defects.” For example, are they in fact defects? Do they change the composition and, if so, how? How might they influence fibrosity? Grain size? What effects might their relatively larger spaces have on trace-element contents? Are they growth or alteration products?

HIGH-RESOLUTION TEM IMAGES AND ATOMIC-FORCE MICROSCOPY

(the photos for this problem were taken by Huifang Xu)

4. Alkali feldspars: surface and bulk structures

Diffraction measurements are probably the most common approach to determining mineral structures, but direct visual methods have had increasing appeal as methods for imaging methods at the near-atomic scale have improved. Such direct imaging is especially useful when studying crystal defects, twinning, and other deviations from ideality.

Here we consider the effects of Al-Si ordering and twinning in alkali feldspars. We will use electron diffraction, high-resolution TEM imaging, and atomic-force microscopy.

Each spot on a diffraction pattern (DP) represents a set of parallel planes in a crystal. The DP spots can be represented by the Miller indices of the diffracting planes, except that no parentheses are used in diffraction (or “reciprocal”) space. Thus, the diffraction spot from the (*hkl*) planes has indices *hkl* in the DP. The separation between (*hkl*) planes can be determined from the reciprocals of the separation of (*hkl*) diffraction spots, corrected for the appropriate angles if $\alpha, \beta, \gamma = 90^\circ$.

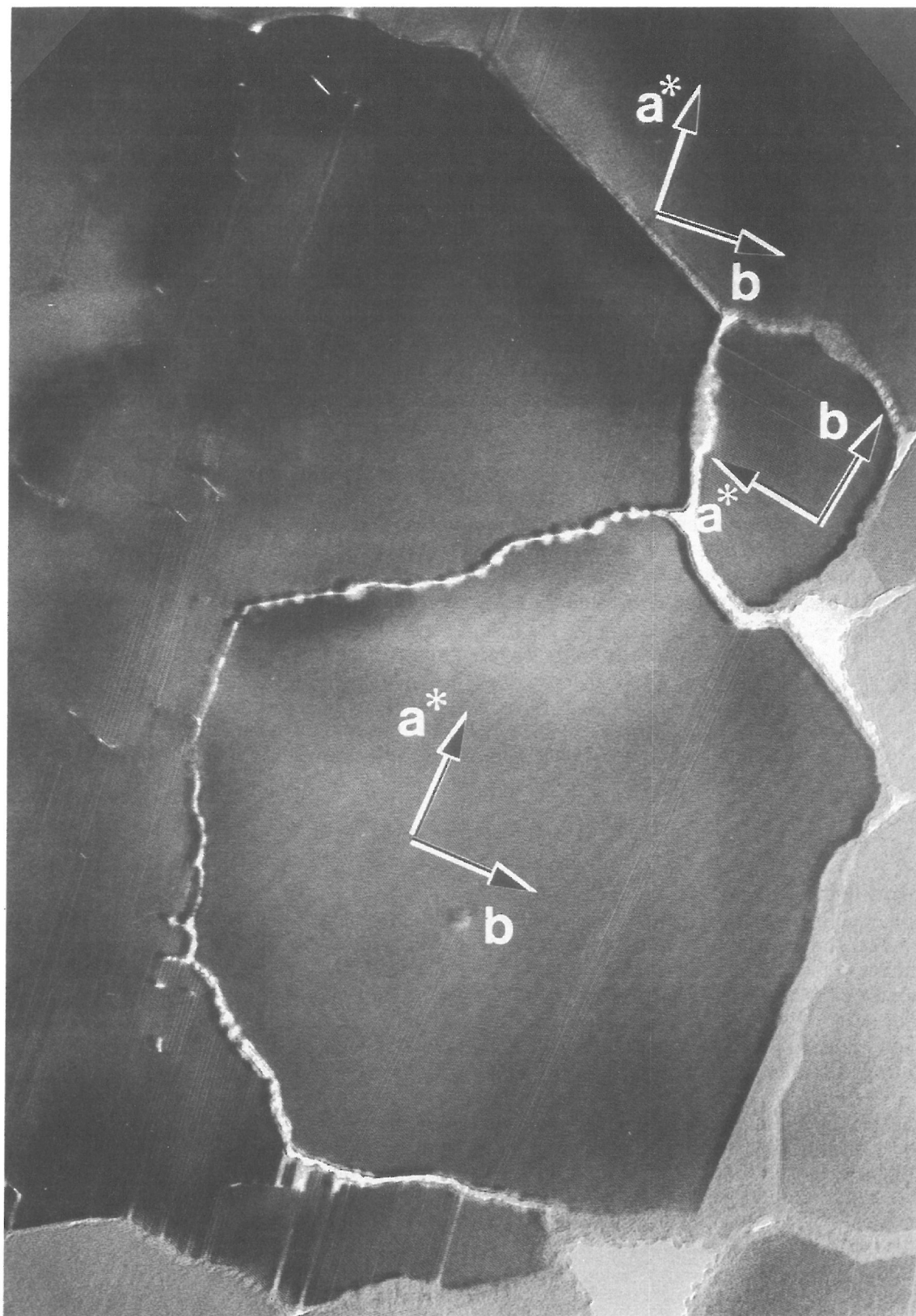


Figure 3a. HRTEM image of crocidolite.

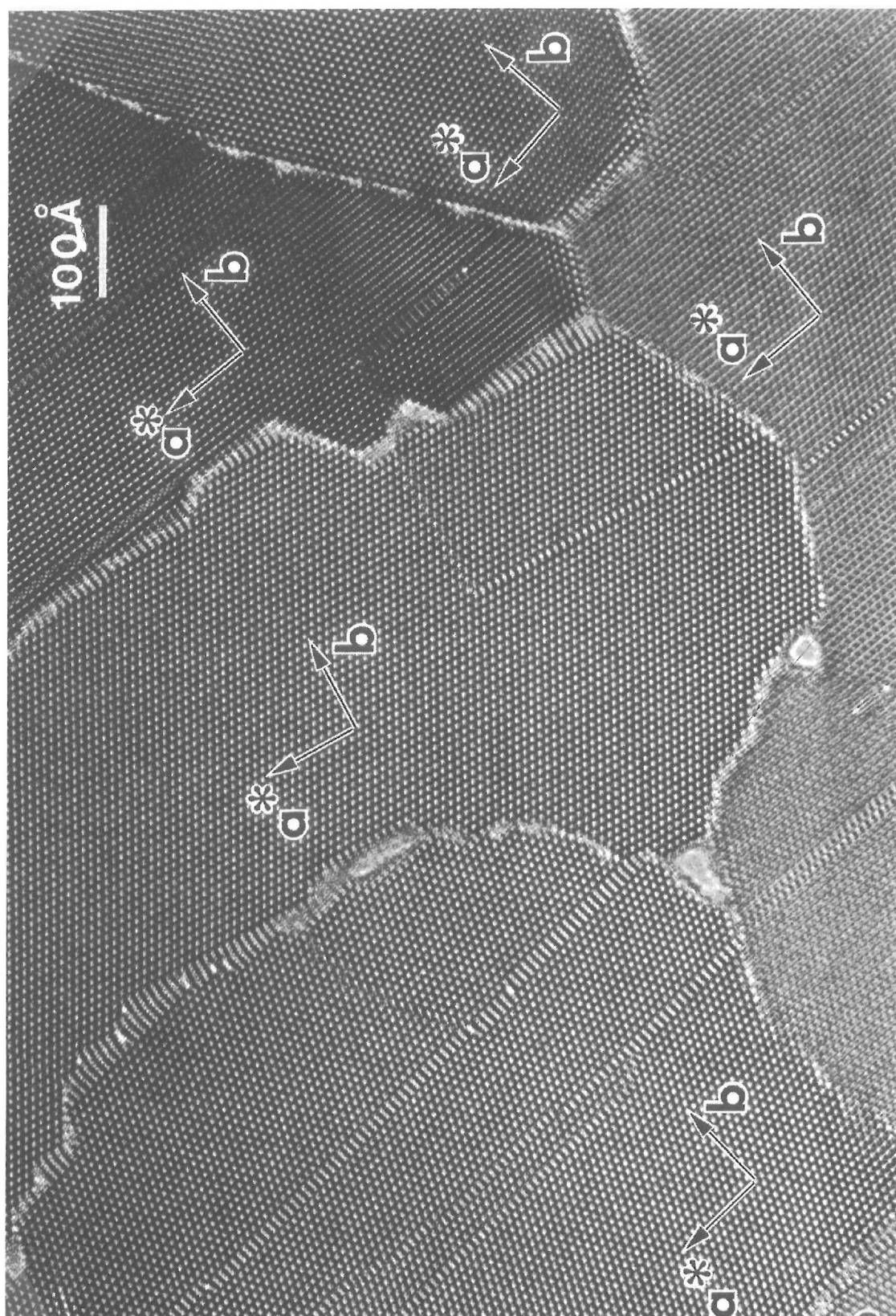


Figure 3b. HRTEM image of crocidolite.

An $a^* - b^*$ electron-diffraction pattern of feldspar is shown in Figure 4a. It provides information about the interplanar spacings of the $(h00)$ and $(0k0)$ sets of planes and the angles between them. Photographic processing has produced minor distortions, so measurements can have errors of a few percent.

- a) **Electron diffraction** Using a metric ruler, determine the separations in mm of the spots along the vertical and horizontal directions. These are directly proportional to the interplanar spacings in nanometers.

For the crystal that yielded this DP, these directions turn out to be parallel to crystallographic axes.

- [1] Using the ratio of the spacings along these directions (i.e., the distance from the 000 spot representing the center of the DP and the position of the radiation beam), and the values in the following table, determine which crystallographic axis is horizontal and which is vertical.

Values for a sodic K-spar of the appropriate composition:

$a = 0.84 \text{ nm}$ $b = 1.30 \text{ nm}$ $c = 0.72 \text{ nm}$ $\alpha, \gamma = 90^\circ$ $\beta = 116^\circ$

- [2] Give the Miller indices and spacings of the crystal planes perpendicular to the crystallographic directions determined above.
[3] What is the zone axis for this diffraction pattern?

- b) **HRTEM imaging** Consider the high-resolution image (Figure 4b) of the crystal studied above.

- [1] Two sets of planes are dominant in the HRTEM image: those that slant NE-SW and those that slant NW-SE. From the information developed in a), what are the indices of these planes?
[2] The image shows three lamellae; the ones at the top and bottom are of the same mineral (and are truncated along their lengths). The arrows indicate the positions of twin planes (slightly shaded). From what you know of feldspar and its twinning, which is orthoclase and which is albite (actually potassic albite)?
[3] Confirm your estimates from measurements of the enlargement and your knowledge of the relative dimensions of Na and K.
[4] What might cause the “scalloping” along the boundary (most prominent in the box) between the two minerals? How is it related to the twinning?

- c) **AFM (surface) microscopy** The atomic-force image (Figure 4c) shows the surface configuration of the sample studied above. Note that we now see a 3-D image of the projection illustrated in b), above. The images are not from the identical regions shown in the HRTEM image and so the K/Na ratios may differ slightly. As a result, the lamellae widths also differ slightly.

- [1] Which are the more Na-rich (albitic) lamellae and which are of orthoclase?
[2] What are the widths (~wavelengths) of the lamella?

The sample displays a peristeritic optical effect (a greenish yellow iridescence) that results from the diffraction of light from the intergrowths. Are the twin or the exsolution lamellae the most likely sources of this optical effect? Explain your reasoning.

- [3] Locate and mark the surface steps.

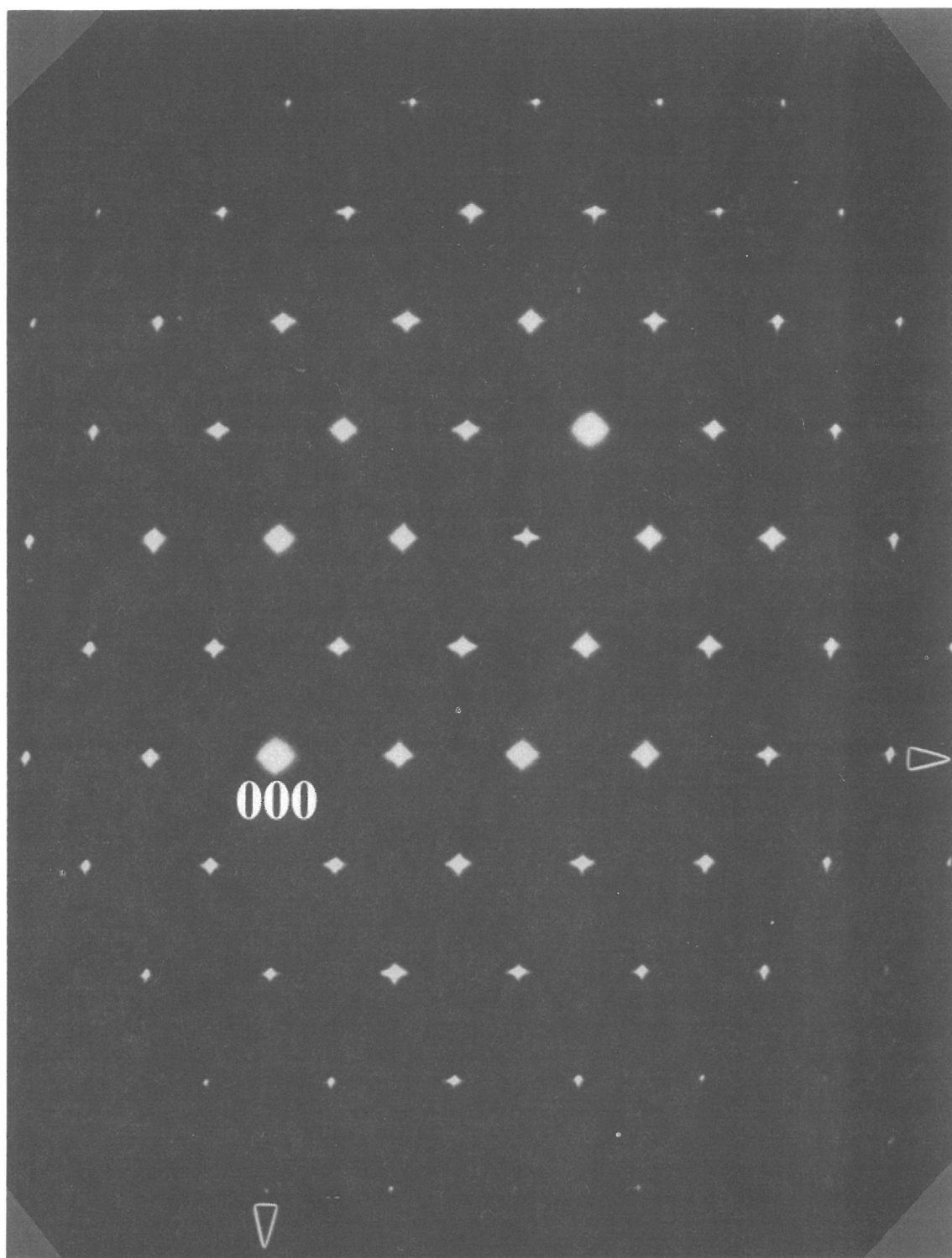


Figure 4a. $a^* - b^*$ electron diffraction pattern of feldspar.

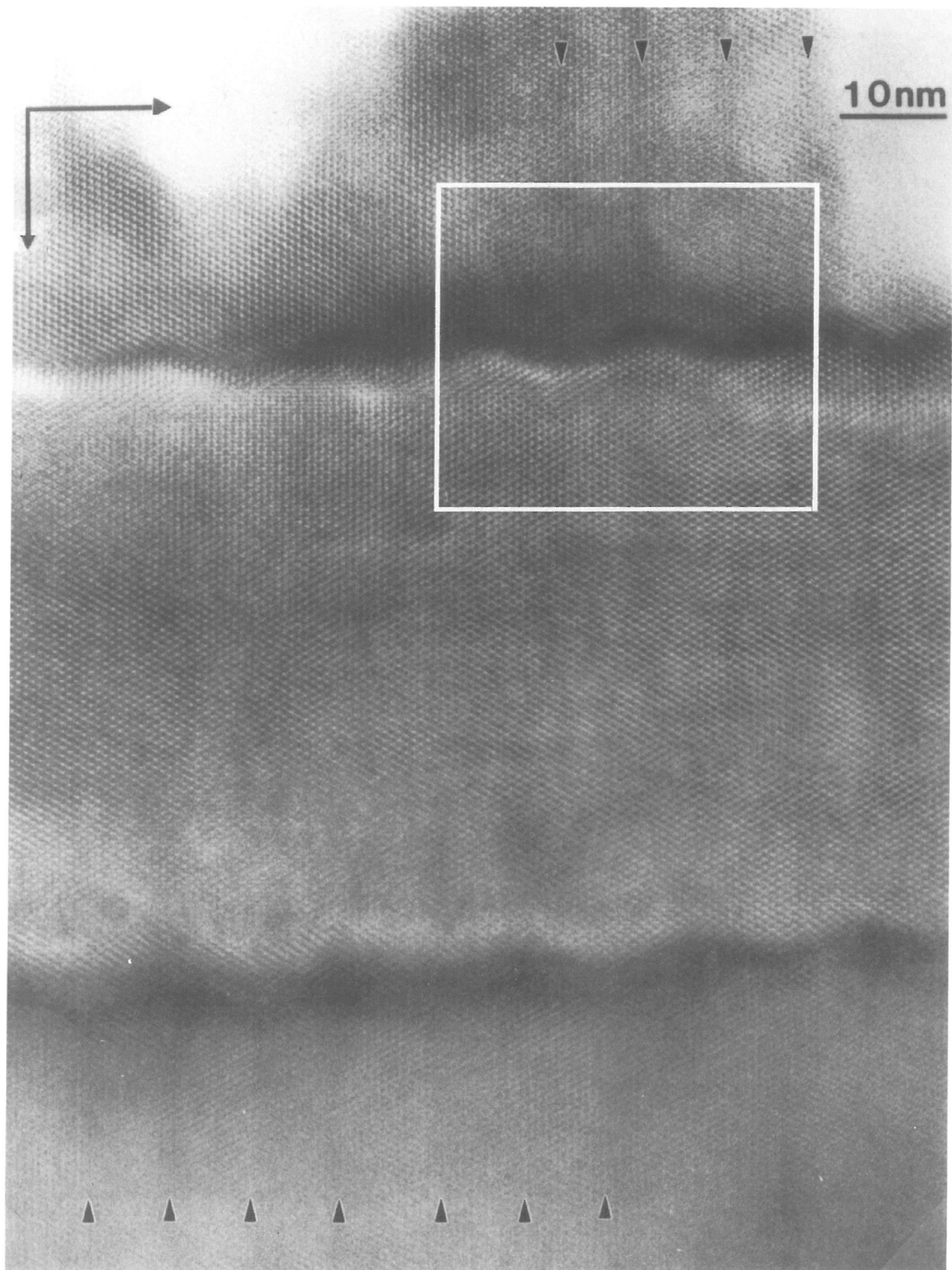


Figure 4b. HRTEM image of feldspar.

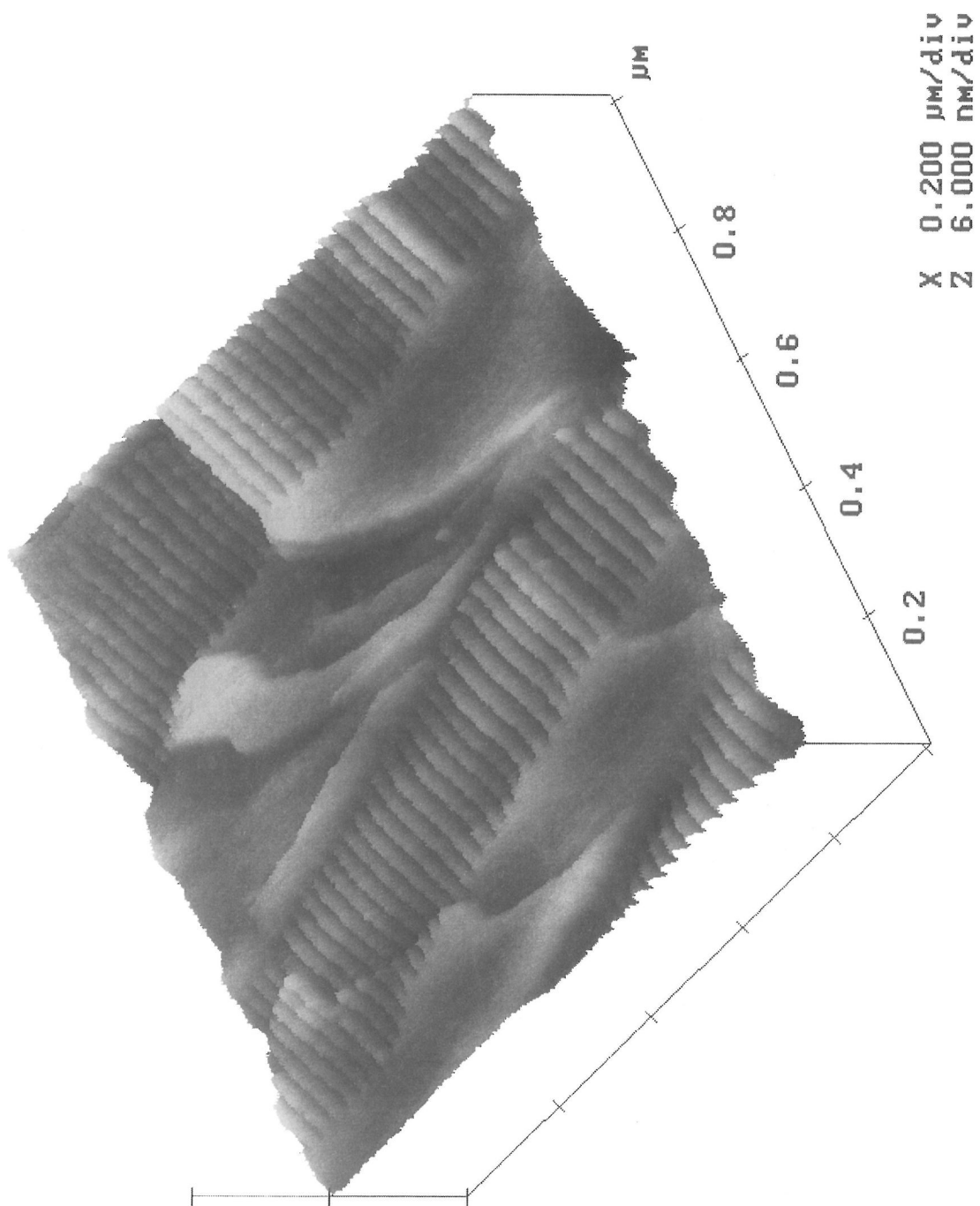


Figure 4c. AFM image of feldspar.

ANSWERS for "FROM 2D to 3D: II. HRTEM and AFM IMAGES"

1. a) there are 6-fold rotation axes in the centers of the channels, 3-folds at along the long body diagonal at $1/3$, $2/3$ and $2/3$, $1/3$, and 2-folds in the center of the cell and in the centers of each cell edge;
 b) the unit cell has a rhombic shape;
 c) problemite contains one lattice node while cordierite is centered, i.e., it contains two nodes;
 d) hexagonal.

2. a) [1] if the differences in intensity are ignored, then a unit cell can be defined; such differences are harder to overlook for the digenite than for the bornite; [2] there are horizontal and vertical m's, and 2- and 4-folds in bornite but none in the digenite image; [3] bornite: #3 – "Unicorns" (Escher #78); #4 – "Iselberg"; digenite: "Birds in Space" provides a fairly good match. The clustered vacancies give rise to superstructures.
 b) [1] The modulations make it difficult to define a unit cell; it would need to be large enough to include a full wave and would then be considered a supercell. [2] The small squares define the PbS layer. [3] The modulations of #6 – "Birds in Space" by Escher probably provides the best match.
 c) [1] The variations in site occupancies make it difficult to define a unit cell; [2] Cells containing a site with less than a full complement of Fe atoms, i.e., those with a black (unoccupied) site in its center, are superstructure cells that are larger than the subcells; [3] The best analogy to the presumed point defects are probably provided by "Shells and clams" (Escher #42), although where they are ordered into superstructures problems #3 – "Unicorns" (Escher #78) and #4 – "Iselberg" may be applicable. Clearly, there is scope for discussion.
 d) [1] The combination of Mg and Ca have a lower mass and therefore lower electron density than does Ca alone, and therefore the columns that contain Mg plus Ca will have lower contrast. [2] The Ca/Mg ordering produces an enlarged unit cell (a small superstructure) and so roughly resembles that in #3 – "Unicorns" (Escher #78) and #4 – "Iselberg."

3. a) [1] Their "zippers" are in view and are almost exactly parallel, and so we assume the two grains have almost identical orientations. [2] Their orientational relations and "lock and key" type of intergrowth suggests that the smaller grain is being "calved" from the larger one. [3] Fibers seem to form from larger grains.
 b) [1] The angular mismatch varies but is only a few degrees for most fibers. [2] Wide chain pyribole on its way to forming a layer silicate such as a mica.

4. a) [1] The two axes in this pattern are \mathbf{a}^* and \mathbf{b}^* . \mathbf{b}^* is horizontal and \mathbf{a}^* is vertical. [2] And along \mathbf{a}^* : 200 (0.42 nm), 400 (0.21 nm), ... and along \mathbf{b}^* : 020 (0.65 nm), 040 (0.325 nm), ... Extinct reflections are of type $h00$ and $0k0$, where h and k are odd. The zone axis is $[001]$.
 b) [1] The NE-SW set of planes correspond to (110), while those that slant NW-SE correspond to $(1\bar{1}0)$. [2] The lamellae at top and bottom contain fine albitic twins and serve to identify this mineral as albite, while the central lamella is the "orthoclase." [3] The spacings of the planes in the potassic material are slightly larger, reflecting the greater diameter of K than Na. [4] The scalloping is produced by the interfaces of the albitic twins with the potassic feldspar (not a very adequate explanation!).
 c) [1] The average widths are ~12 nm and ~2 nm. [2] The twin lamellae define the albite and the broader lamella are the "orthoclase."

A FUN AND EFFECTIVE EXERCISE FOR UNDERSTANDING LATTICES AND SPACE GROUPS

Dexter Perkins

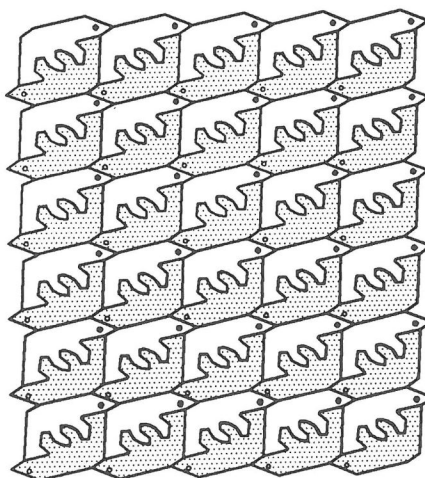
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Introduction

In 1996, Peter Buseck presented a laboratory exercise based on Escher drawings (see MacGillavry 1965) at the Teaching Mineralogy Workshop (Smith College, June 1996). Buseck's exercise (a version of which is included in this book) is an excellent way to learn about two-dimensional symmetry, especially symmetry involving translation. It was fun for all the mineralogists present, but some of its most significant lessons dealt with concepts that may be beyond the scope of a basic mineralogy course. Buseck's ideas excited me, and I recalled that, in 1981, Francois Brisse wrote an article entitled "*La Symétrie bidimensionnelle et le Canada*" (*Two dimensional symmetry and Canada*) which included some beautiful and fascinating color figures based on motifs representative of Canada, the Canadian Provinces and Canadian Territories. Brisse's figures are just as spectacular as Escher's but are simpler for students to analyze.

Brisse's thirteen pictures are brightly colored and contain motifs of fish, boats, flowers, buffalo, polar bears and other things representative of Canada. The lowest symmetry pattern, titled "New Brunswick," has symmetry $p1$ and contains a motif of a Viking ship with sails. A polar bear pattern ("Northwest Territories") has symmetry $p2$ (Figure 1); patterns of maple leaves ("Canada") and pacific dogwood ("British Columbia") belong to tetragonal space groups. In all, Brisse's patterns represent thirteen of the seventeen possible two-dimensional space group symmetries. They exhibit rotational axes, mirror planes, and glide planes. Most unit cells are primitive, but two are centered. The only problem with using Brisse's patterns is that he ignored color when he determined their symmetry. When color is considered, most have less symmetry than Brisse indicates--see the polar bear pattern, below.

Figure 1. Polar bear pattern modified and redrafted from one of Brisse's figures. Brisse gives the symmetry as $p2$, but if the white and stippled polar bears are considered to be different, it has symmetry $p1$.



The Exercise

The exercise that follows is based on Brisse's figures. My students have found it to be an excellent way to learn about plane symmetry and to understand space groups. Although this exercise only involves two dimensions, students seem to have little difficulty applying the same principles to three dimensions. Before using the exercise, during a semester I would typically give three to five lectures on translational periodicity and space groups. Now, I allow students to spend two class periods on this project and follow with a one hour discussion and wrap-up session. Although some cooperative learning projects seem to be inefficient ways to cover material, this is one example of how group exercises can save time. Students learn the same things more efficiently and have more fun while they are doing it.

Pedagogical Notes

Symmetry can be an intimidating and confusing subject, so students should not be left on their own to do this exercise. They will have the most fun and success if they work in groups of two or three individuals, and if they do all their work in class so they can interact with other groups. I give them minimal instructions possible, but am always present if they have questions. The student groups present their findings and conclusions to the whole class at appropriate times while they are doing the exercise---not just during our wrap-up session. Often I assign different parts of this project to different groups: each group then becomes the experts in something. Different groups sometimes get different results, in part because symmetry is sometimes ambiguous, and consequently we have some lively discussions. In particular, the students like to debate whether Brisse correctly or incorrectly gives the symmetry of his Saskatchewan pattern as *cm*.

This exercise is based on discovery learning. Students need little introduction to lattices and space groups. They can figure things out for themselves. For example, they will figure out what a glide plane is, and if you tell them ahead of time it takes away from the learning experience. The last question, which asks them to make their own symmetrical drawings, is difficult but often leads to some spectacular results.

Canadian Mineralogist originally published the figures for this exercise in color, and the exercise is best done with color reproductions. However, some of Brisse's patterns can be reproduced adequately in black and white. I caution instructors, however, to be aware of applicable copyright laws.

References

- Buseck, P.R., 1996, Escher patterns and crystal defects: *Proceedings of the Teaching Mineralogy Workshop*, Smith College, June 1996, p. 44-64.
- Brisse, F., 1981, La symétrie bidimensionnelle et le Canada: *The Canadian Mineralogist*, v. 19, p. 217-224.
- MacGillavry, C.H., 1965, *Symmetry Aspects of M.C. Escher's Periodic Drawings*: International Union of Crystallography.

Plane Lattices, Space Groups and the Flags of Canada

We have given you *patterns* based on the flags of Canada and Canadian Provinces. They contain *motifs* that systematically repeat to fill two-dimensional space. These drawings come from an article in *Canadian Mineralogist* (vol. 19, pp 217-224, 1981) by François Brisse: *La symétrie bidimensionnelle et le Canada*. The motifs are:

Canada: maple leaf
Prince Edward Island: map of the island
Northwest Territories: polar bear
Nova Scotia: sail boat
British Columbia: pacific dogwood flower
Yukon: fireweed flower
Newfoundland: cod fish
Saskatchewan: wheat sheaf
Ontario: trillium flower
Alberta: wild rose
Manitoba: buffalo
New Brunswick: Viking ship
Quebec: fleur de lis: flower

1. Two-dimensional patterns may have one of seventeen possible symmetries, called two dimensional *point groups*. The Canadian patterns represent thirteen of them. For each:
 - a. Put a piece of tracing paper over the pattern. Choose one point on the diagram and put a dot there, and then put dots at all the other identical points on the diagram. (Pay attention to color, the direction something is pointing, etc.--the points must be identical in all ways.) The pattern of points is a *lattice* describing the *translational symmetry* of the pattern.
 - b. On your lattice drawing, show all symmetry elements that the lattice has. Use solid lines for mirrors; small lens shapes for 2-fold axes; small triangles for 3-fold axes, small squares for 4-fold axes; small hexagons for 6-fold axes. Also on your drawing, choose two vectors that generate the whole lattice from one initial point. By convention you should choose short vectors, and vectors at special angles like 90° , 60° , etc. if you can.
 - c. Choose four near-neighbor lattice points related by the vectors you just chose to define a parallelogram. The four points outline a *unit cell* that repeats many times to make the entire pattern. The vectors you chose, and the lattice, describe the way the unit cells repeat. Draw one unit cell and show all its symmetry using the same symbols as in part b, above.
 - d. Finally, put tracing paper over the pattern again, and show all the symmetry elements of the entire pattern. First do this ignoring color (as Brisse did) and then do it again paying attention to color. Neither may yield the same symmetry elements as the lattice. How do the symmetries of the lattice, the unit cell and the entire structure (ignoring color) compare? What if you consider color--how do they compare then?

(Suggestion: you might want to work on all the patterns that appear to have "square" properties first, then go on to the hexagonal or rectangular ones, etc.)

2. Ignoring color, which of the Canadian patterns have 2-fold (or 4-fold or 6-fold, which include 2-fold) axes of symmetry? Which of the lattices have 2-fold (or 4-fold or 6-fold) axes of symmetry? Why are your answers the same, or not the same, for both questions?
3. The two-dimensional patterns can have any of seventeen different symmetries, but unit cells can have only five basic shapes. They correspond to five different lattices with five different symmetries. What are they? What symmetries do they have?
4. According to Brisse, the Canadian patterns all have different symmetries (listed in Table 1; Brisse ignored color when determining symmetry). Consult Table 1 and look at all the patterns with numbers in their symmetry symbols. What do the numbers mean? Similarly, what does *m* mean? And, more difficult, what do the symmetries containing “*g*” have in common? What do you think “*g*” means? Finally, what about the “*p*” or “*c*” that appears as the first element in the symbols--what do they mean? (This is a tough question.) Why do you suppose there is a “1” in some of the symbols?
5. Brisse’s drawings are for thirteen of the possible seventeen two-dimensional space groups. Here’s a tough task: make your own drawings for the other four space groups. To make your task simpler, and to make it easier to see, use a simple motif composed of circles, dots, squares, etc. Then, for one of the four space groups, try to make something that looks more like one of Brisse’s drawings.

Table 1. Plane group symmetries. The table below lists the seventeen possible two-dimensional point groups and space groups. You will find this chart useful for this exercise.

<u>lattice</u>	<u>point group</u> (unit cell symmetry)	<u>space group</u> (structure symmetry)	<u>Canadian patterns</u>
oblique (<i>p</i>)	1	<i>p1</i>	New Brunswick
	2	<i>p2</i>	Northwest Territories
rectangular (<i>p</i> or <i>c</i>)	<i>m</i>	<i>pm</i>	-----
	<i>m</i>	<i>pg</i>	Nova Scotia
	<i>m</i>	<i>cm</i>	Saskatchewan
	<i>2mm</i>	<i>p2mm</i>	-----
	<i>2mm</i>	<i>p2mg</i>	Manitoba
	<i>2mm</i>	<i>p2gg</i>	Newfoundland
	<i>2mm</i>	<i>c2mm</i>	-----
square (<i>p</i>)	4	<i>p4</i>	Prince Edward Island
	<i>4mm</i>	<i>p4mm</i>	British Columbia
	<i>4mm</i>	<i>p4gm</i>	Canada
hexagonal (<i>p</i>)	3	<i>p3</i>	-----
	<i>3m</i>	<i>p3m1*</i>	Alberta
	<i>3m</i>	<i>p31m*</i>	Quebec
	6	<i>p6</i>	Ontario
	<i>6mm</i>	<i>p6mm</i>	Yukon Territories

*In *p3m1*, the *m*irror lines bisect the 60° angles between cell edges; in *p31m*, the reflection lines coincide with the cell edges.

CONSTRUCTION OF CRYSTAL MODELS AND THEIR GRAPHIC EQUIVALENTS

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INTRODUCTION

This laboratory exercise involves construction of physical and computer models of crystals based on a description of their symmetry. The purpose of the exercise is to help you visualize symmetry in two and three dimensions, and to help you explore the relationships between the different crystal systems. It is a problem-solving exercise: the morphology of the crystal is described in simple terms, and both physical and computer models should meet the requirements of these descriptions. Because the physical models may be used in other laboratory exercises, they should be large enough and precise enough for measurement, and durable enough to take handling.

Materials

The physical models can be built from any reasonably durable material. Heavy paper (used manila folders, for example) works well for models up to about 5 cm edge length. A fast-setting glue that is compatible with the materials being used is necessary.

Computer models can be made with programs for making crystal drawings (*e.g.*, SHAPE). The only requirement is that the program be flexible enough to allow input based on crystal morphology (*i.e.*, the program should not require specification of the space group).

Assignment

1. For parts 1 and 2 of this assignment, you will work in groups. Each group is responsible for making two physical models of each of three crystals you are assigned. The two models may be identical, or may be different, if different geometries satisfy the requirements.

Leave one model of each pair blank; on the second, mark the locations of the symmetry elements (except symmetry centers), and label each face with its Miller index and the name of the form to which it belongs.

Your group number is in the top line of the following table; the models you will make are specified by the entries (columns) in the table.

Group No.	1	2	3	4	5	6
No. of Faces:	4	4	4	4	4	4
Crystal System:	triclinic	monoclinic	orthorhombic	tetragonal	hexagonal	isometric
No. of Faces:	5	5	5	5	5	5
Crystal System:	triclinic	monoclinic	orthorhombic	tetragonal	hexagonal	isometric
No. of Faces:	6	6	6	6	6	6
Crystal System:	triclinic	monoclinic	orthorhombic	tetragonal	hexagonal	isometric

2. Using SHAPE, make computer models of each crystal you made in assignment 1. Print out appropriate graphics for each.

3. When you have completed 1 and 2, turn in your results, so that everybody has access to your models and crystal drawings. Then each of you will write and hand in an essay discussing the following:

How are objects of a specific crystal system, but having 4, 5 and 6 faces, related to each other?

How are objects having the same number of faces, but belonging to different crystal systems, related to each other?

Can you name minerals that have crystals shaped like the models?

In your essay, you should use proper crystallographic terminology, and illustrate the principles involved using stereographic projections of appropriate crystals. The text of your essay should be limited to one typewritten page for each question.

Grading

Each group will be assigned a grade for models and graphics. This group grade will be 50% of the grade for the exercise. Grades for the essay will be the other 50% of the grade.

NOTES TO THE INSTRUCTOR

This laboratory exercise is designed to achieve three objectives: 1. to fix in students' minds the essential symmetry content of the six crystal systems; 2. to help students visualize the relation between three-dimensional objects and their two-dimensional representations; and 3. to help students understand the relationships between the six crystal systems. Students should see that lower symmetry objects can be visualized as distortions of higher symmetry objects; this is particularly obvious among the crystals with six faces.

There are four activities in this exercise. Some are best planned as group activities. The first is the construction of physical models that meet specific requirements and correspond to the symmetry of the six crystal systems. The second is the construction, using a computer program like SHAPE, of a two dimensional representation of the physical model that was built in step 1. The third is a writing activity that requires students to compare models of the different crystal systems using crystallographic terminology. The fourth is an optional activity that extends the first two by requiring students to identify, on their models, the symmetry elements that are present, the Miller indices of specific faces, the forms that are present, and to draw stereographic projections. I regard the first and third activities as essential to the exercise.

I can think of three ways of assigning groups. Pairs of students can be assigned to complete pairs of physical and computer models. Groups of students can be assigned to make all models for a single crystal system, or groups of students can be assigned to make all models meeting specific constraints, regardless of the crystal system to which they belong. Once the models are made, they become community property, to be used by all students for completing the third activity.

The background students require to complete this exercise is an introduction to symmetry and to the crystal systems. If the fourth activity is assigned, introduction to Miller indices, forms and stereographic projection is also needed. I have not tried this exercise exclusively as a “discovery” exercise in which students have no prior introduction to symmetry and crystal systems, although I think this approach might also be possible. Even after an introduction to crystal systems, there is a problem solving aspect to the exercise that frightens some students: the simple recipe describing the crystal morphology is difficult for most students to translate into a series of adjoining faces that have to be cut and folded, etc. Most students assemble the crystals from separate pieces, rather than planning out a strategy for making the model from a single, contiguous piece. It is helpful to point out that the students need to leave “tabs” along the edges of the crystal faces so that adjacent faces can be glued together.

One of the models that is assigned - an object with five faces and isometric symmetry - is, to the best of my knowledge, impossible to build. Students assigned this model will discover that it is impossible. Assigning this model is a useful teaching exercise because of its discovery aspect.

Left to their own devices, students generate a variety of products: some models will be less than an inch on a side, others will be the size of a basketball; some will be made of onionskin paper with no integrity of shape, others will be of balsa wood; some will be nondescript, others will have each face a different color; some will be very precisely made, others will hardly have parallel edges or regular angles. If all of the models are within an acceptable range of durability, these differences are useful for talking about shape and size in contrast to form and symmetry.

I schedule this exercise over three laboratory periods, involving an aggregate of 3 hrs of scheduled laboratory time. I assign it and introduce SHAPE on Tuesday (1.5 hr lab period), work and consult with students Thursday (1.5 hr lab period), collect models the following Tuesday, and collect essays Thursday. I expect the essays to be done outside of scheduled lab time, so that the second week, except for brief discussion of some of the models on Tuesday, is available for introduction of new material.

I found the assignment involving SHAPE to be difficult. When I assigned this, we had DOS version 2; I found it not to be user-friendly, and the distortion of crystal shapes in some of the perspectives was hard to explain to students. I use parts of this exercise as a take-home activity for K-6 science teachers in an introductory earth science course, with good results. The exercise is easily exportable to younger students, and teaches solid geometry in a simple, hands-on way.

BUILDING CRYSTAL STRUCTURE BALL MODELS USING PRE-DRILLED TEMPLATES: SHEET STRUCTURES, TRIDYMITE, AND CRISTOBALITE

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OVERVIEW¹

Ball models have long been used as teaching tools in Mineralogy to illustrate molecular and crystal structures. At Union College, Mineralogy students construct crystal structure ball models to help them better understand the concepts of crystalline order, relative atomic size, atomic coordination, crystal chemistry, and crystal symmetry. We have used two methods for this:

- 1) The students each choose a mineral (an ionic compound) to work on during the second half of the term. They research the mineral origin, occurrence, chemistry, properties, and structure, and write a report. Part of the report is a model of one or more unit cells of the mineral, built using glued together 1/8" to 1" diameter metal and plastic balls (everything from ball bearings to marbles to tennis balls can be successfully used, provided they can be firmly stuck together). The students must choose ball sizes so that they properly fit into the various sites using the radius ratio concept for ionic coordination polyhedra. This type of project has been reasonably successful, but the ball models do not always work out well.

The first problem is that many structures are too difficult for most undergraduates (or me) to build. Garnet and quartz, for example, are two that may look easy, but turn out to be very difficult to build. A related problem is that most silicate and oxide structures are not simple arrays of atoms, like the intersections of lines on graph paper. Small differences between ball radii and the effective (scaled) ionic radii of the real atoms, or small displacements of the balls from atomic positions in the real structures, often result in grossly distorted models. For example, the isometric spinel minerals can be thought of as being based on a cubic closest packed array of oxygens, with the oxygen layers perpendicular to a unit cell body diagonal. In principal, all one should have to do is make the oxygen layers, adding cations in the appropriate places as you go. However, all of the spinel models that have come from these student projects are trigonal.

Several different methods have been used to glue the spheres in the proper places: rulers, clay supports, tape supports, graph paper grids, custom ruled grids, computer drawings, constructing simple subunits of the structures and then combining them, and others. In most cases these methods do not work well since they are not accurate enough or cannot be applied accurately enough. I thought that using pre-drilled templates would allow the straight-forward construction of a limited set of structures, but structures that at least could be successfully built. Since the object is to learn about crystal structures, rather than about model construction techniques, I thought the tradeoff was reasonable.

¹ Sources of the materials we use are given in the Appendix.

- 2) I had two kinds of templates machined: a packed hexagonal array (Figure 1) used for making octahedral layers with $\frac{1}{2}$ " spheres as oxygens or hydroxyls, and an extended hexagonal array (Figure 2) for making corner-sharing tetrahedral layers with $\frac{1}{2}$ " spheres as oxygens. In one 3-hour lab session students use the templates to build various sheet silicate components. The models are then used with sheet mineral hand samples and other props to show the origin of strong pleochroism, the systematics of stacking polytypes, and the reasons for differences in hardness. The models are useful for teaching principles of X-ray diffraction, because the sheets can be stacked and measured to show why the basal spacings of the sheet structures differ. The sheet components that the students make are brucite, serpentine, and talc. These can make brucite, serpentine, talc, biotite (requires some loose K atoms), chlorite, and various clays. Offsets of the paired hydroxyls in the octahedral layers of talc or biotite make it easy to show sheet stacking vectors and the ordering of stacking polytypes. Stacking polytypes can also be demonstrated with oriented layers of Plexiglas® hexagons (Figure 3).

The models are fully extended hexagonal sheets, not the less extended trigonal sheets that are so common in nature. Trigonal templates are much harder to design and machine. All of the octahedral layers we make are trioctahedral, since the octahedral vacancies of dioctahedral sheets make the final models too fragile for routine classroom use.

Using templates to make sheet silicate models is easy, accurate, fast, and reliable. Three years of Mineralogy students, working in groups of two, have successfully built their one or two model components in one lab session, with time to spare for discussion of crystal structure, stacking, and using mineral specimens as examples of how properties change with structure (note that each group needs its own templates, so make plenty). The only serious problem has been with excess glue dripping down and cementing the model to the template. This problem can be solved by making the templates of plastic that is resistant to Duco® cement, such as polyethylene or polypropylene, instead of Plexiglas®. Wood has been tried as a template material, but it is too difficult to make sharp, clean edges on the holes, and so ball locations are not accurate enough. Hot-melt glue guns, for gluing the balls together, have been found by others to work well. Glue guns do not have potentially toxic solvents and the glue cures in seconds, but minor burns are possible. Some glue guns are quite inexpensive.

As the years go by, sheet silicate models accumulate. The individual sheet components are not very useful or instructive, so I do not give them away to the students who made them (although giving away colorful models to students may be good advertising for geology programs). Instead, I keep some model sets for use outside of Mineralogy. Scout troops, for example, love them during mineral demonstrations. I gave away one set (two of each kind of sheet) to a high school earth science teacher, and that is probably what I will continue to do.

What else can the templates be used for? In principal they can be used for any structure that can be approximated by hexagonal arrays of oxygens and/or by fully extended hexagonal tetrahedral layers. Two examples that I include below are tridymite and cristobalite, which are easily made using only the tetrahedral layer template. Reasonably accurate ilmenite and hematite models can easily be made using the octahedral template, although the distorted octahedra will not be distorted in quite the right way. Olivine, spinel, and most other structures based on closest packed arrays of oxygens usually cannot be properly made with these templates. This is because the template octahedra are extended in a plane parallel to the layer to fit the fully extended hexagonal tetrahedral layers in sheet silicates. As a result, the octahedra are strongly flattened perpendicular to the layers. If you want to make olivine and spinel, drill an octahedral template like

that shown in Figure 1, but make the line spacings 0.380" instead of 0.433" for " balls. You will also have to use six-coordinated spheres that have diameters of 5/16" rather than the 7/16" spheres used here for the sheet silicates.

Crystal and Structural Chemistry of Common Sheet Silicates

All of the common sheet silicates and related minerals are based on two principal components: tetrahedral layers and octahedral layers.

Tetrahedral layers

The tetrahedral layers are nominally hexagonal arrays of corner-sharing SiO_4 tetrahedra. In most natural sheet silicates, small rotations of the Si-O-Si bonds result in arrays that have trigonal symmetry. The shared oxygens in the layer are called "bridging oxygens", since they are the bridges that link adjacent SiO_4 tetrahedra. The other oxygens are called "apex oxygens", since they occupy the 'free' apex of each tetrahedron. Apex oxygens are all shared with cations in the octahedral layer. In talc and some other sheet silicates, Si^{4+} occupies all of the tetrahedral sites. In other sheet silicates Al^{3+} replaces usually $\frac{1}{3}$ but up to $\frac{2}{3}$ of the Si^{4+} ions.

Octahedral layers

The octahedral layers are composed of edge-sharing octahedra, and the layers come in two varieties. In trioctahedral layers all octahedra are occupied, usually by divalent cations such as Mg^{2+} . In dioctahedral layers only $\frac{2}{3}$ of the octahedra are occupied, usually by Al^{3+} .

Connected octahedral and tetrahedral layers

Octahedral layers can be bare, can be attached to a tetrahedral layer on one side, or can be sandwiched between two tetrahedral layers. Bare octahedral layers are obviously not silicates, but since they are layer structures related to and in some cases combined with other layer types, they are included here. In bare octahedral layers, such as brucite, all of the anions are hydroxyls rather than oxygens to maintain charge balance. Each 6-coordinated cation is bonded to 6 hydroxyls. We will ignore the hydrogens of the hydroxyls in our models. The stacking sequence for pure octahedral layer minerals is $\text{O} \sim \text{O} \sim \text{O} \sim \text{O}$, where O represents octahedral sheets stacked up parallel to c, and '~' represents weak hydrogen bonds between the sheets.

If the octahedral layer is connected to one tetrahedral layer, as in the 2-layer sheet silicate serpentine, then $\frac{2}{3}$ of the hydroxyls on *one* side of the octahedral layer are replaced by oxygens. These are the apex oxygens of the tetrahedral layer that are shared between the tetrahedral and octahedral layers. Each 6-coordinated cation is bonded to 2 oxygens and 4 hydroxyls. The stacking sequence for 2-layer silicates is $\text{T-O} \sim \text{T-O} \sim \text{T-O} \sim \text{T-O}$, in which T represents tetrahedral layers, O represents octahedral layers, '-' represents strong bonds within the sheets, and '~' represents weak hydrogen bonds between the sheets.

If the octahedral layer is sandwiched between two tetrahedral layers, as in the 3-layer sheet silicates talc, then $\frac{2}{3}$ of the hydroxyls (as in brucite) on *both* sides of the octahedral layer are replaced by tetrahedral layer apex oxygens. Each octahedral cation is then bonded to two hydroxyls and four oxygens. Again, the oxygens are shared between the octahedral and tetrahedral layers. The stacking sequence for 3-layer sheet silicates is $\text{T-O-T} \sim \text{T-O-T} \sim \text{T-O-T}$, with the symbols as defined above, except that '~' here represents weak Van der Waals bonds in talc or stronger ionic bonds in micas where K, Na, or Ca occupy the interlayer sites.

Systematic crystal structural chemistry

The table below summarizes the common sheet silicates and related minerals, as distinguished by layer type, layer stacking, and layer composition. The A-site is the 10 to 12 coordinated site nested between the 6-sided rings of facing tetrahedral layers. The A-site may contain K^+ , Na^+ , Ca^{2+} , and other large low-charge ions, and o (vacancies).

Stack	Layers	A-site	Diocahedral	Triocahedral
~O~	1-layer	None	Gibbsite $\{Al_2\}\{OH\}_6$	Brucite $\{Mg_3\}(OH)_6$
~O-T~	2-layer	None	Kaolinite $\{Al_2\}\{Si_2O_5\}(OH)_4$	Serpentine $\{Mg_3\}[Si_2O_5](OH)_4$
~T-O-T~	3-layer	\square	Pyrophyllite $\square\{Al_2\}\{Si_4O_{10}\}(OH)_2$	Talc $\square\{Mg_3\}[Si_4O_{10}](OH)_2$
~T-O-T~	3-layer mica	K^+	Muscovite $K\{Al_2\}\{AlSi_3O_{10}\}(OH)_2$	Biotite (Phlogopite) $K\{Mg_3\}[AlSi_3O_{10}](OH)_2$
~T-O-T~ O~	4-layer	None	None?	Chlorite $\{Mg_3\}[Si_4O_{10}](OH)_2 \cdot \{Mg_3\}(OH)_6$

T = Tetrahedral layer in the stack.

O = Octahedral layer in the stack.

{ } = Octahedral layer cations in the formulae.

[] = Tetrahedral layers in the formulae.

The coupled substitution $3^{[6]}M^{2+} \Leftrightarrow 2^{[6]}Al^{3+} + [6]\square$ controls the composition difference between dioctahedral and trioctahedral structures. The coupled substitution $^{[12]}\square + ^{[4]}Si^{4+} \Leftrightarrow ^{[12]}K^+ + ^{[4]}Al^{3+}$ controls the composition difference between 3-layer sheet structures having empty (e.g., talc) vs. occupied (e.g., biotite) A-sites. Na^+ , and Ca^{2+} are major A-site ions in some micas. A common substitution in micas, chlorite, and some serpentines is the coupled substitution $^{[6]}Mg^{2+} + ^{[4]}Si^{4+} \Leftrightarrow ^{[6]}Al^{3+} + ^{[4]}Al^{3+}$ (the Tschermak substitution), which makes most micas and chlorite more Al-rich than the basic formulae. Many medium-size ions can substitute in the octahedral sites, including Fe^{2+} (almost universal), Ni^{2+} , Co^{2+} , Fe^{3+} , V^{3+} , Cr^{3+} , Li^+ , and Ti^{4+} . Obviously some substitutions are simple and some are coupled, depending on the ion and the sheet silicate into which it is substituting. No ions other than Si^{4+} and Al^{3+} are abundant in tetrahedral sites.

Stacking polytypes

Despite the nominally hexagonal shape of the sheets, sheet silicates do not generally have hexagonal symmetry. First, tetrahedral layers must usually shrink a little to fit the more rigid octahedral layers. Tetrahedral layers do this by slight rotations of Si-O-Si bridging oxygen bonds, becoming trigonal in the process. Second, paired hydroxyls and tetrahedral layers on either side of each octahedral layer in micas and talc are offset from one another (Figure 4). Each sheet, therefore, has an intrinsic polarity known as the stacking vector (Figure 5). The vectors of stacked sheets may all point in the same direction in a crystal, or they may point in different directions in a repeating pattern or randomly up the stack (the c axis; Figure 6). Sheet silicates that are identical but for the stacking vector repeat pattern are polymorphs, but are referred to as polytypes since they are physically almost identical to one another. X-ray diffraction, however, can spot the characteristic repeat spacing of the stacking vector. There are six simple types of stacking vector repeats, presented in the table below and in Figure 6.

Polytype name	Sheets/ repeat	Crystal system	Stacking vector rotation/layer	Symmetry element $\parallel c$
1M	1	Monoclinic	none	mirror.
2M ₁	2	Monoclinic	60°	c glide.
2M ₂	2	Monoclinic	120°	c glide.
2O	2	Orthorhombic	180°	c glide.
3T	3	Trigonal	120°	3 ₁ screw axis
6H	6	Hexagonal	60°	6 ₁ screw axis
M _d	Disordered	Monoclinic	Disordered	mirror

Look in a mineralogy text to see which minerals commonly have which stacking polytypes.

Building the Models: Instructions to Students

Sheet silicates

Sheet silicates are among the easiest silicate models to make. Most sheet silicates do not have perfect hexagonal arrays, but rather are slightly distorted with trigonal symmetry. Even in the rare sheet silicates with perfectly hexagonal arrays (e.g., the Fe-rich biotite annite), the sheets stack to yield monoclinic, trigonal, orthorhombic, or hexagonal crystals. Our models will have completely extended, perfectly hexagonal arrays since it makes no difference to the symmetry of the final crystals, and it makes the models easier to build.

You will work in teams of two building parts for a variety of trioctahedral sheet structures. It is not difficult to build accurate models, since most of the atoms will be located using precisely machined templates. The glue tends to be a bit of a mess. Do your best to keep glue off the templates, and keep paper towels handy to wipe up excess glue. Each team will build parts of various sheet structures, including 3-layer talc sheets, 2-layer serpentine sheets, and 1-layer brucite sheets. Using these components, and unglued K⁺ ions, we will be able to construct a variety of mica, clay, and hydroxide structures. Dioctahedral sheet silicates are easy to build in principle, but in practice the models are too fragile.

Gluing is the hardest part of making ball models. The best way to do it is to put a ball in place first to see where it makes contact with others. Then remove the ball, put small blobs of glue at the contact points, and fit it back together. Make sure the glue is at the contact points, and leave the glue to dry. Don't let the glue drip down onto the template.

Atoms and the balls that represent them are shown in Figure 7. For talc, follow the instructions in Figures 8 to 12. For serpentine, follow the instructions in Figures 8, 13, and 14. For brucite, follow the instructions in Figures 13 and 15.

In the serpentine and talc models one tetrahedral layer is completely removable from the octahedral layer. This allows you to see how oxygens are shared between layers, and to see the 6-coordinated ions that are otherwise hidden. A-site vacancies of talc can be filled with loose K⁺ ions to make biotite.

Tridymite and Cristobalite

Tridymite and cristobalite are polymorphs of silica, SiO_2 . They are two of the nine known thermodynamically stable, condensed silica phases (Figure 16): α and β quartz, α and β tridymite, α and β cristobalite, coesite, stishovite, and liquid. Other low-temperature phases that have limited or no true stability fields are moganite and keatite. A new silica polymorph, structurally similar to baddeleyite (ZrO_2), has been predicted on theoretical grounds to be the stable silica polymorph at deep mantle pressures (Belonoshko, et al., 1996).

In their stability fields tridymite and cristobalite can both undergo displacive phase transformations: tridymite from the low temperature trigonal α form to the high-temperature hexagonal β form, and cristobalite from the low temperature tetragonal α form to the high temperature isometric β form. Tridymite also undergoes several metastable polymorphic transformations at temperatures below those of its stability field (Heaney et al., 1994).

The tridymite structure is based on the stacking of alternating layers of corner-sharing silica tetrahedra. Within each layer up- and down-pointing tetrahedra alternate. The layers are stacked so that up-pointing tetrahedra in one layer share oxygens with the down-pointing tetrahedra in the layer above. The layers are arranged to form hexagonal channels parallel to the c crystallographic axis. If you look down the c axis of the structure (Figure 17A), down-pointing tetrahedra of one layer completely hide the up-pointing tetrahedra in the layer below; all the tetrahedral bases are oriented the same way. The structure of hexagonal β tridymite is related to that of lonsdaleite, the hexagonal polymorph of diamond². Silicon in tridymite occupies the same positions as carbon in lonsdaleite, and the oxygens occupy positions corresponding to the C-C bonds.

The cristobalite structure is related to that of tridymite. It, too, is built up of layers of corner-sharing silica tetrahedra, and in each layer up- and down-pointing tetrahedra alternate. However, in cristobalite the layers have three possible positions rather than two, and the hexagonal channels seen in tridymite are blocked. If viewed perpendicular to the layers (Figure 17B), the tetrahedra in one layer are rotated 60° from tetrahedra to which they are linked in the underlying layer. Unlike tridymite, the overlying tetrahedra do not completely hide underlying tetrahedra. Isometric β tridymite has a structure related to that of diamond: silicons occupy the same positions as carbon in diamond, and oxygens occupy positions corresponding to the C-C bonds.

For tridymite, follow the directions in Figures 18 and 19. For cristobalite, follow the directions in Figures 20 to 23. The high-symmetry β polymorphs are made here since templates for them are much easier to design and machine than those for the lower symmetry α polymorphs.

² Lonsdaleite and diamond have structures identical to wurtzite and sphalerite, respectively, if you pretend that all of the atoms in the sulfides are carbon.

General References

- Bailey, S.W., Editor (1984) Micas. Reviews in Mineralogy, v. 13.
Bailey, S.W., Editor (1988) Hydrous Phyllosilicates (Exclusive of Micas). Reviews in Mineralogy, v. 19.

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- Belonoshko, A.B., Dubrovinsky, L.S. and Dubrovinsky, N.A. (1996) A new high-pressure silica phase obtained by molecular dynamics. American Mineralogist, v. 81, p. 785-788.
Klein, C. and Hurlbut, C.S. Jr. (1993) Manual of Mineralogy, 21st Edition. John Wiley and Sons, Inc., New York.
Heaney, P.J., Prewitt, C.T. and Gibbs, G.V. (1994) Silica: Physical Behavior, Geochemistry, and Materials Applications. Reviews in Mineralogy, v. 29, 606 p.
Thompson, J.B., Jr. (1981) An introduction to the mineralogy and petrology of the biopyriboles. In Veblen, D.R., Editor, Amphiboles and Other Hydrous Pyriboles—Mineralogy, Reviews in Mineralogy, v. 9A, p. 141-188.

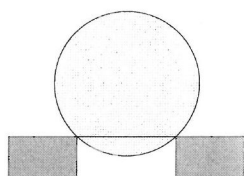
APPENDIX: Sources for Materials

Plastic sheeting:	Plastic spheres:
United States Plastic Corp.	Ace Plastics, Inc.
1390 Neubrecht Rd.	26 North Ave.
Lima, Ohio 45801	Garwood, NJ 07027
800-537-9724.	800-695-4223

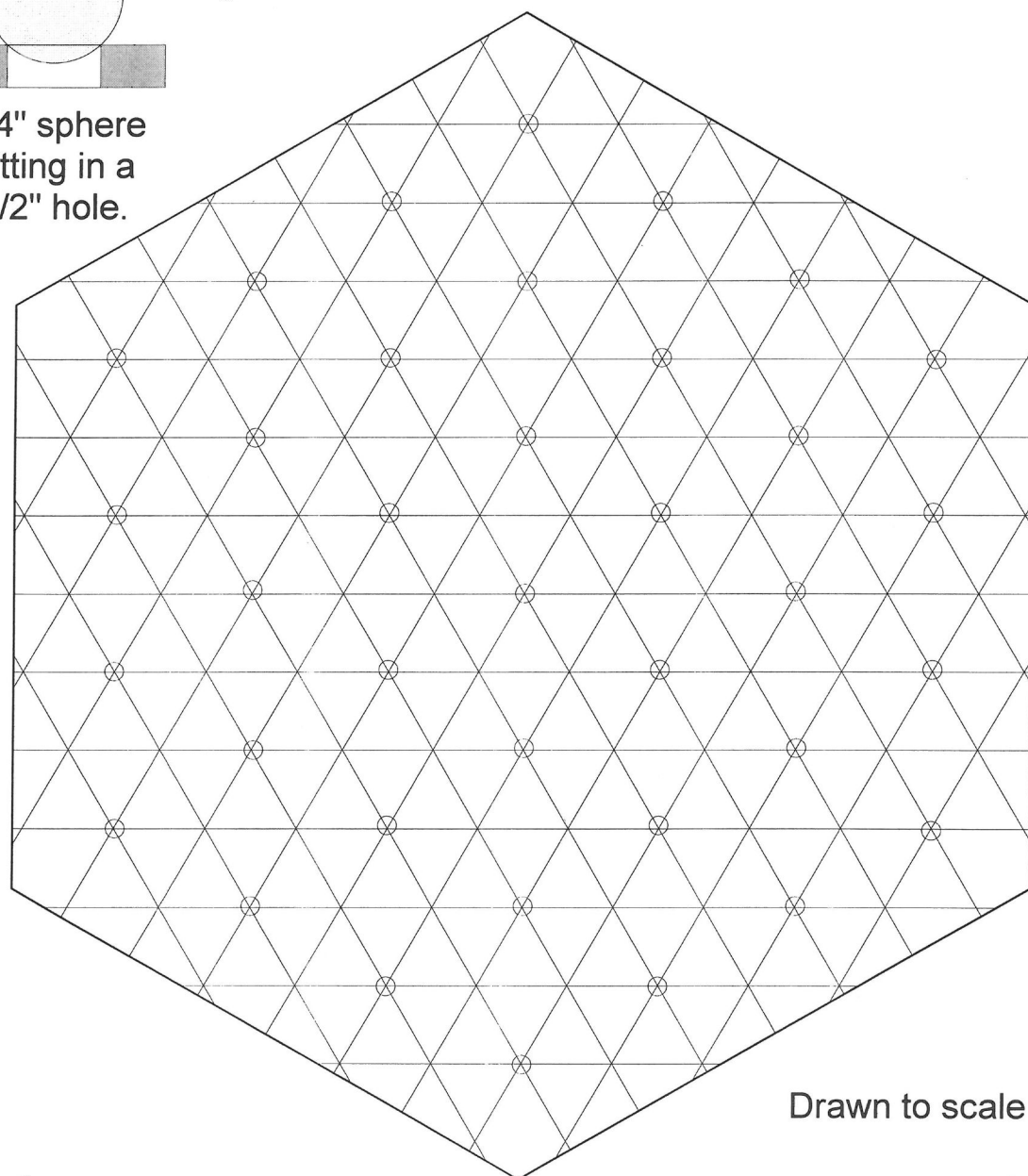
Figure 1. Octahedral layer template for 3/4" spheres.

Material should be 1/4" plastic, preferably polyethylene or polypropylene, or some other plastic to which Duco® Cement does not stick. Plexiglas® works, but models may stick and may be damaged when removed.

1/2" holes should be drilled all the way through the plastic at the positions marked with circles. The lines marking the drill positions are 0.433" apart, and the lines are at 60° angles to one another.



3/4" sphere
sitting in a
1/2" hole.



Drawn to scale

Minimum plastic width 5.5"

Figure 2. Tetrahedral layer template for 3/4" spheres.

Material should be 1/4" plastic, preferably polyethylene or polypropylene, or some other plastic to which Duco® Cement does not stick. Plexiglas® works, but models may stick and may be damaged when they are removed.

1/2" holes should be drilled all the way through the plastic at the positions marked with circles. The lines marking the drill positions are 0.650" apart, and the lines are at 60° angles to one another.

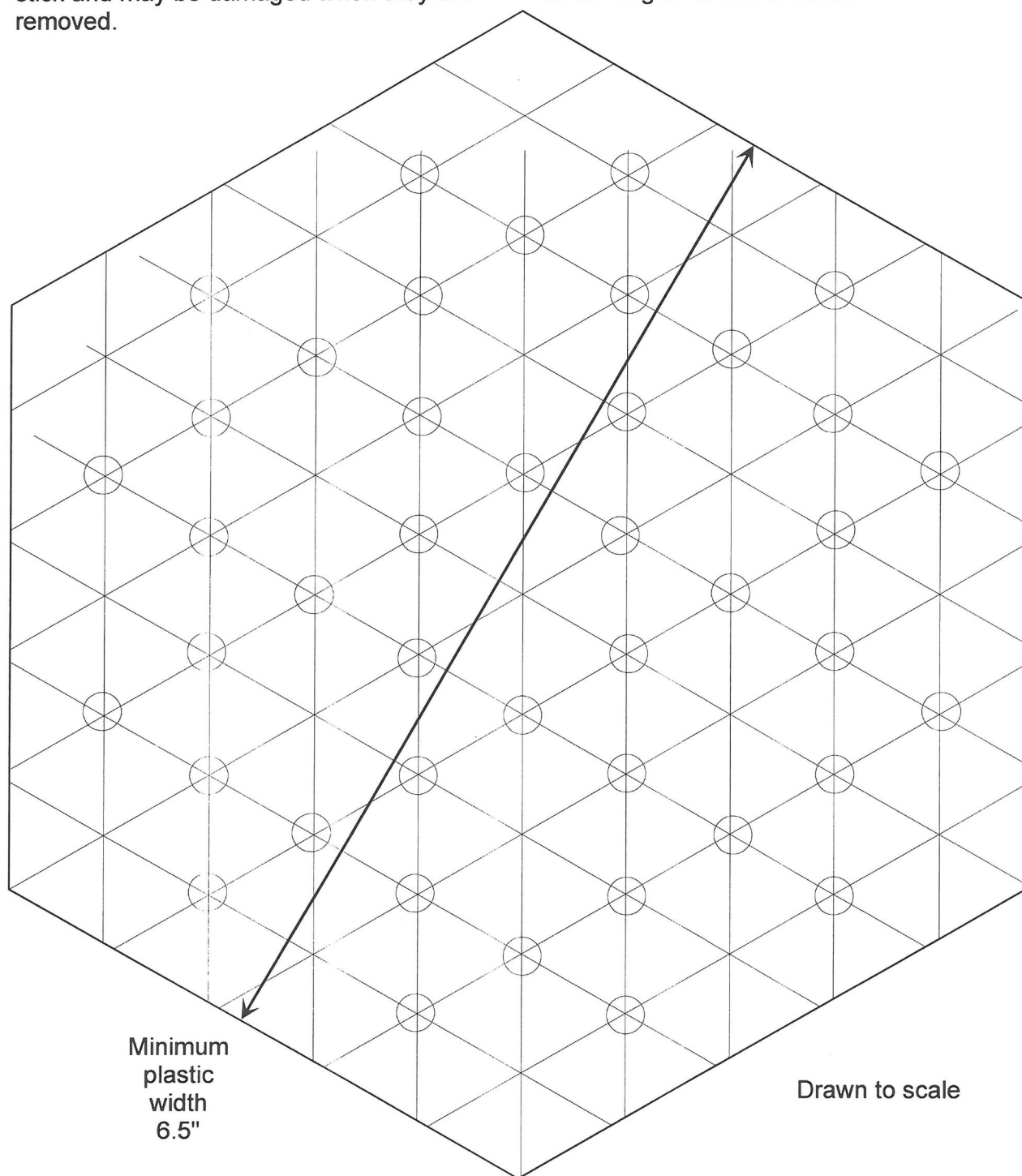
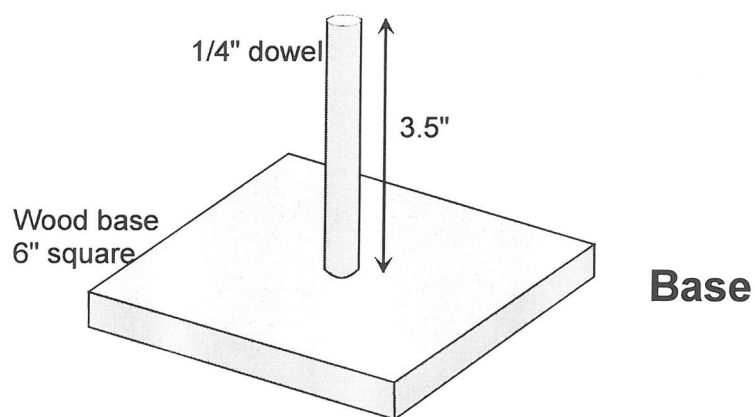
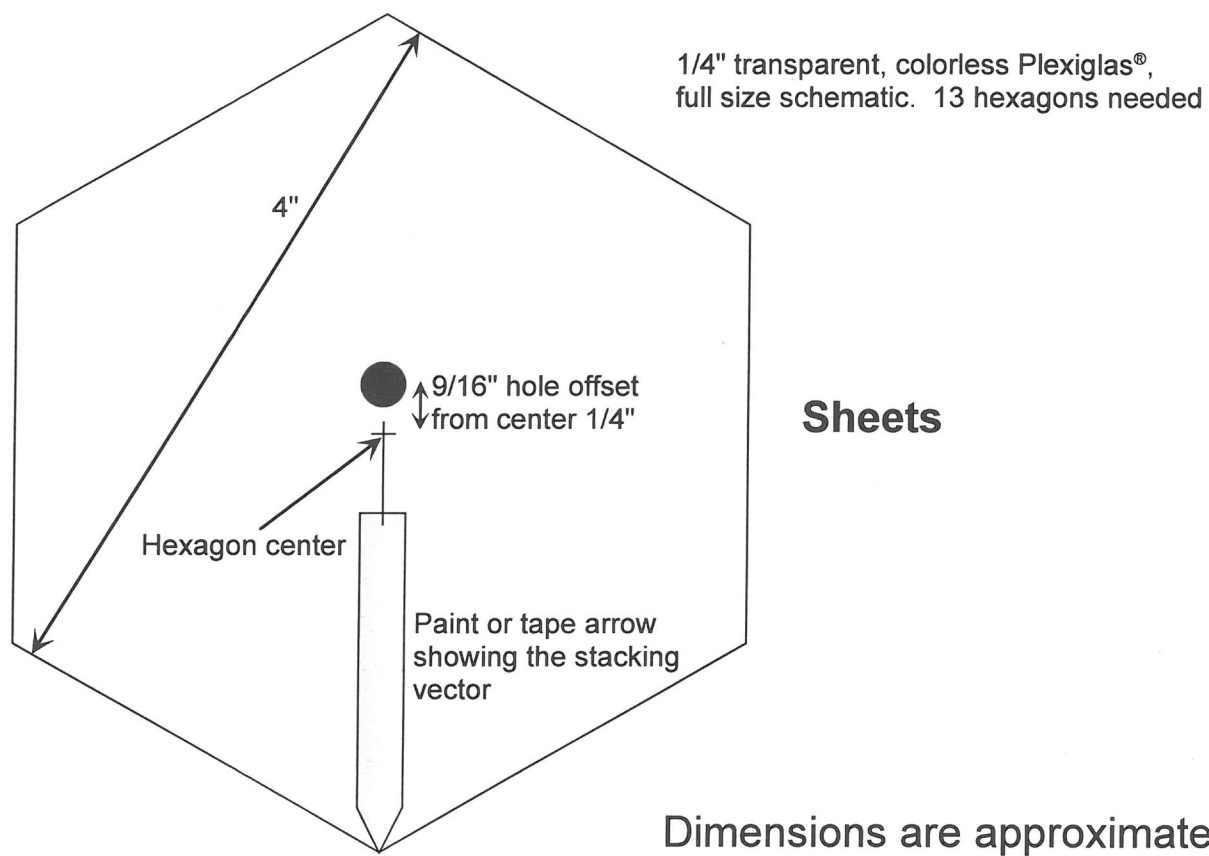


Figure 3. Stacking polytypes demonstration model.



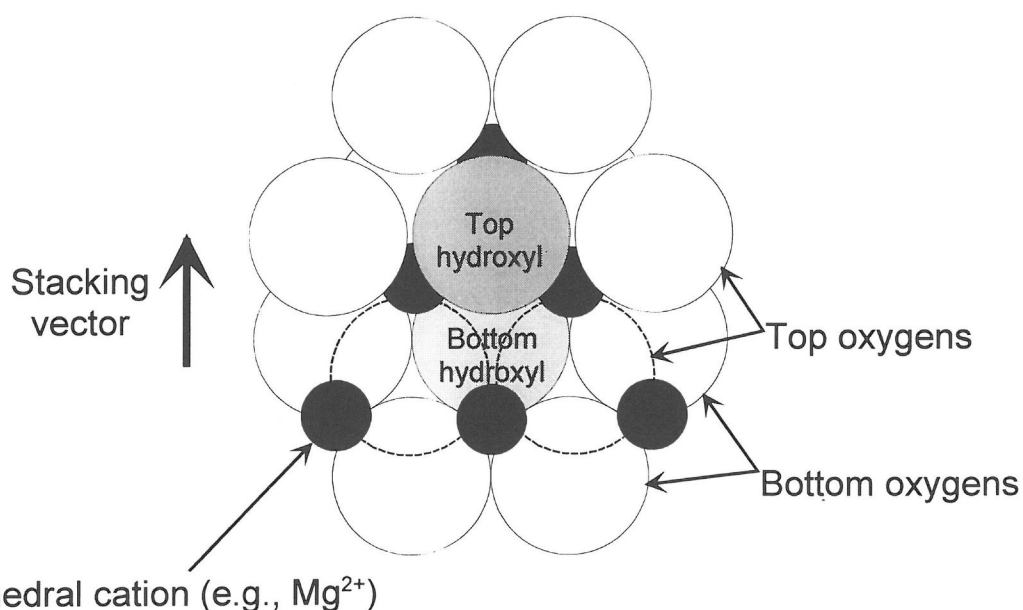


Figure 4. Portion of an octahedral layer in a three layer sheet, showing locations of the hydroxyl pairs. The stacking vector most easily visualized by students is the projection of an arrow that passes from the bottom hydroxyl to the top hydroxyl, as shown.

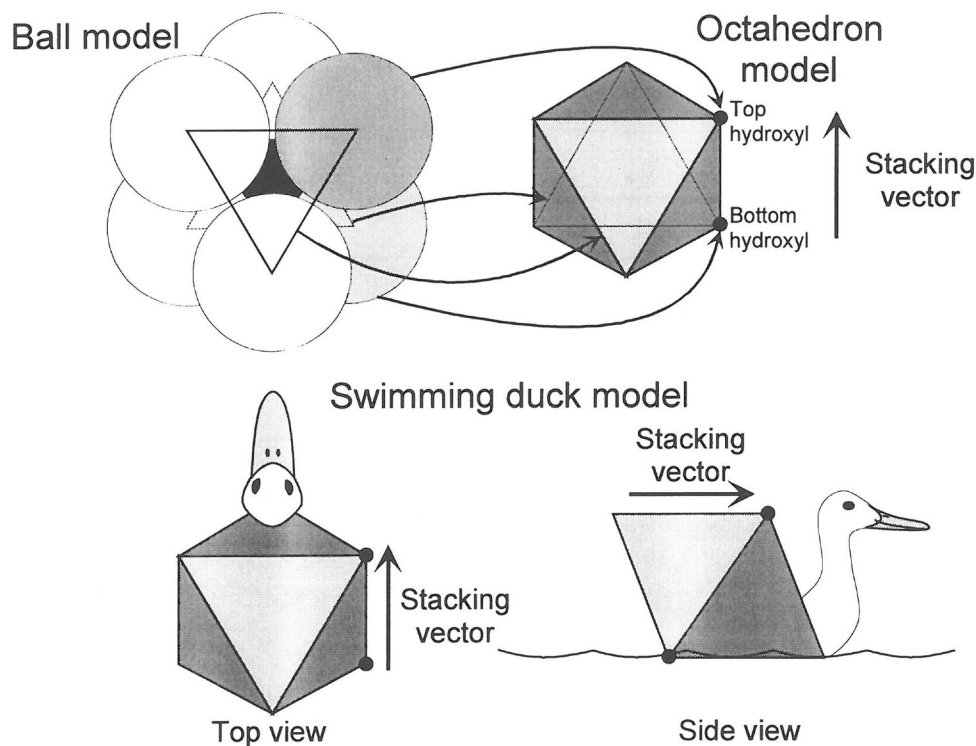
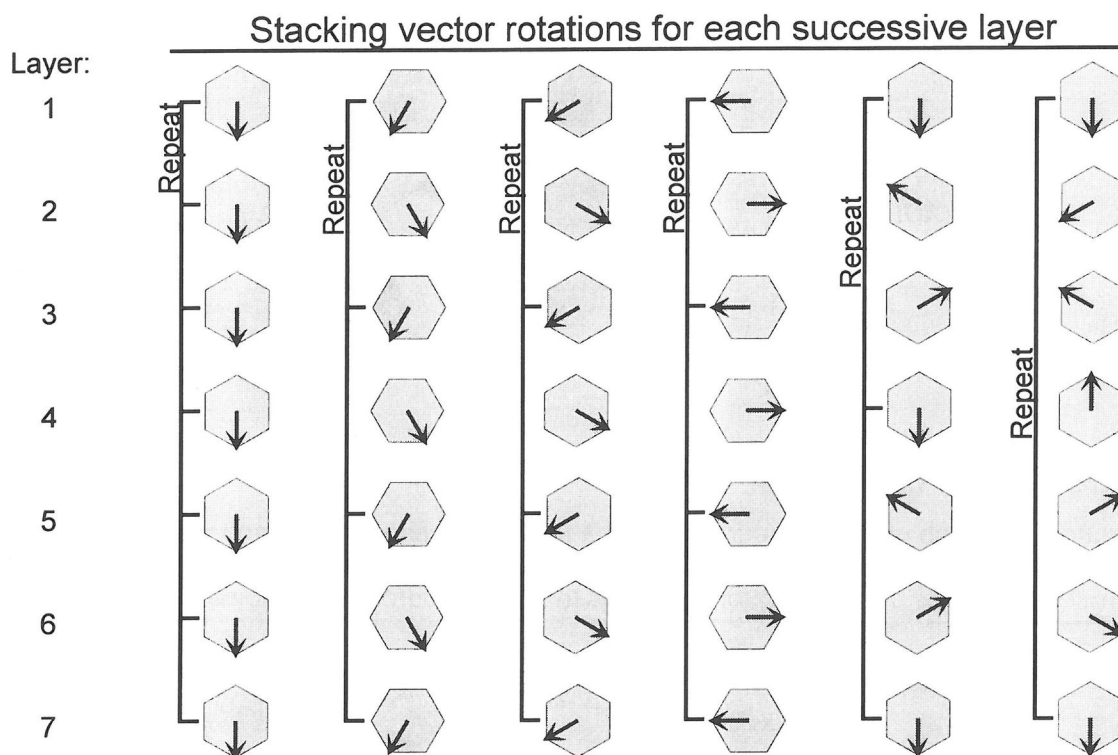




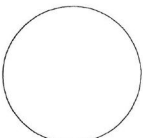
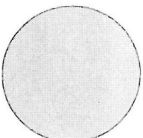
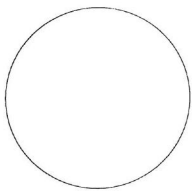
Figure 5. Illustrations of one octahedron in the octahedral layers of three-layer sheets (from the left side of Figure 4). The corners of the octahedron are defined by the atom centers in the ball model. The swimming duck model is a device used to remember the stacking vector orientation based on the hydroxyl offsets (ducks modified after Thompson, 1981).

Figure 6. Sheet silicate stacking polytypes.



Stacking polytype	1M	2M ₁	2M ₂	2O	3T	6H
Layer spacing	10Å	10Å	10Å	10Å	10Å	10Å
Rotation/layer	0°	60°	120°	180°	120°	60°
Layers/repeat	1	2	2	2	3	6
Repeat distance	10Å	20Å	20Å	20Å	30Å	60Å
Nominal X-ray diffraction d-spacings						
{001}	<u>10Å</u>	20Å	20Å	20Å	30Å	60Å
{002}	5Å	<u>10Å</u>	<u>10Å</u>	<u>10Å</u>	15Å	30Å
{003}	3.33Å	6.67Å	6.67Å	6.67Å	<u>10Å</u>	20Å
{004}	2.5Å	5Å	5Å	5Å	7.5Å	15Å
{005}	2Å	4Å	4Å	4Å	6Å	12Å
{006}	1.67Å	3.33Å	3.33Å	3.33Å	5Å	<u>10Å</u>

Figure 7. Types of atoms used in the sheet silicate. models.

-  5/32" steel: Si^{4+} or Al^{3+} in tetrahedral sites
-  7/16" blue plastic: Mg^{2+} in octahedral sites
-  3/4" colorless plastic: Oxygen in tetrahedral or octahedral sheets
-  3/4" orange plastic: Hydroxyls in octahedral sheets
-  1" colorless plastic: K^{+} in interlayer sites

Ball counts for each sheet

Brucite requires 73 OH and 36 Mg

Serpentine requires 66 O, 24 Si, 50 OH, and 36 Mg

Talc requires 132 O, 48 Si, 26 OH, and 36 Mg

Biotite requires a talc sheet plus 7 K atoms

Chlorite requires one talc and one brucite sheet

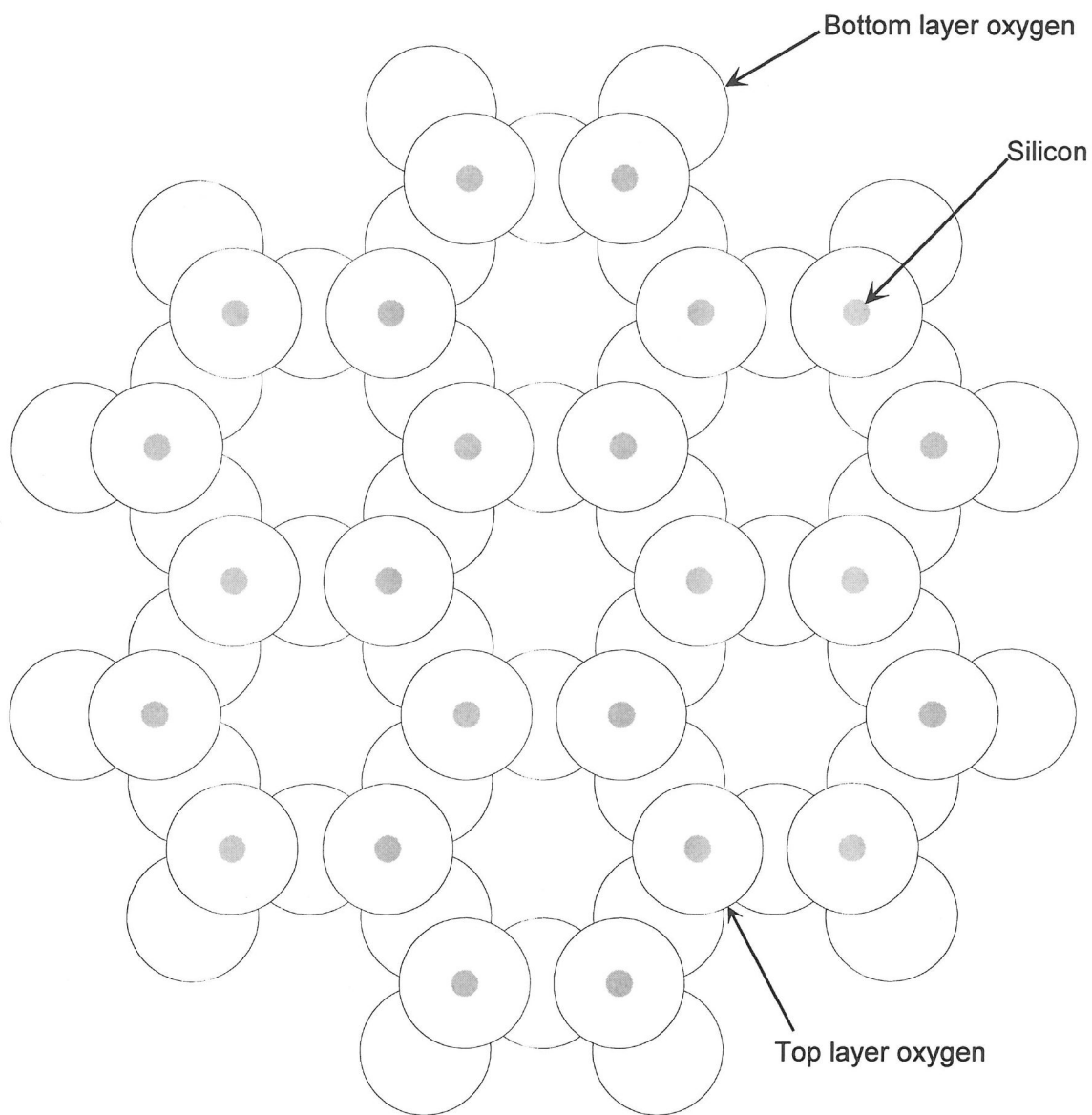


Figure 8. Complete tetrahedral layer for talc or serpentine.

On the tetrahedral template put an oxygen in each position, gluing them together as you go. Then put a silicon over each oxygen triangle. Finally, glue an oxygen over each silicon. This layer is finished.

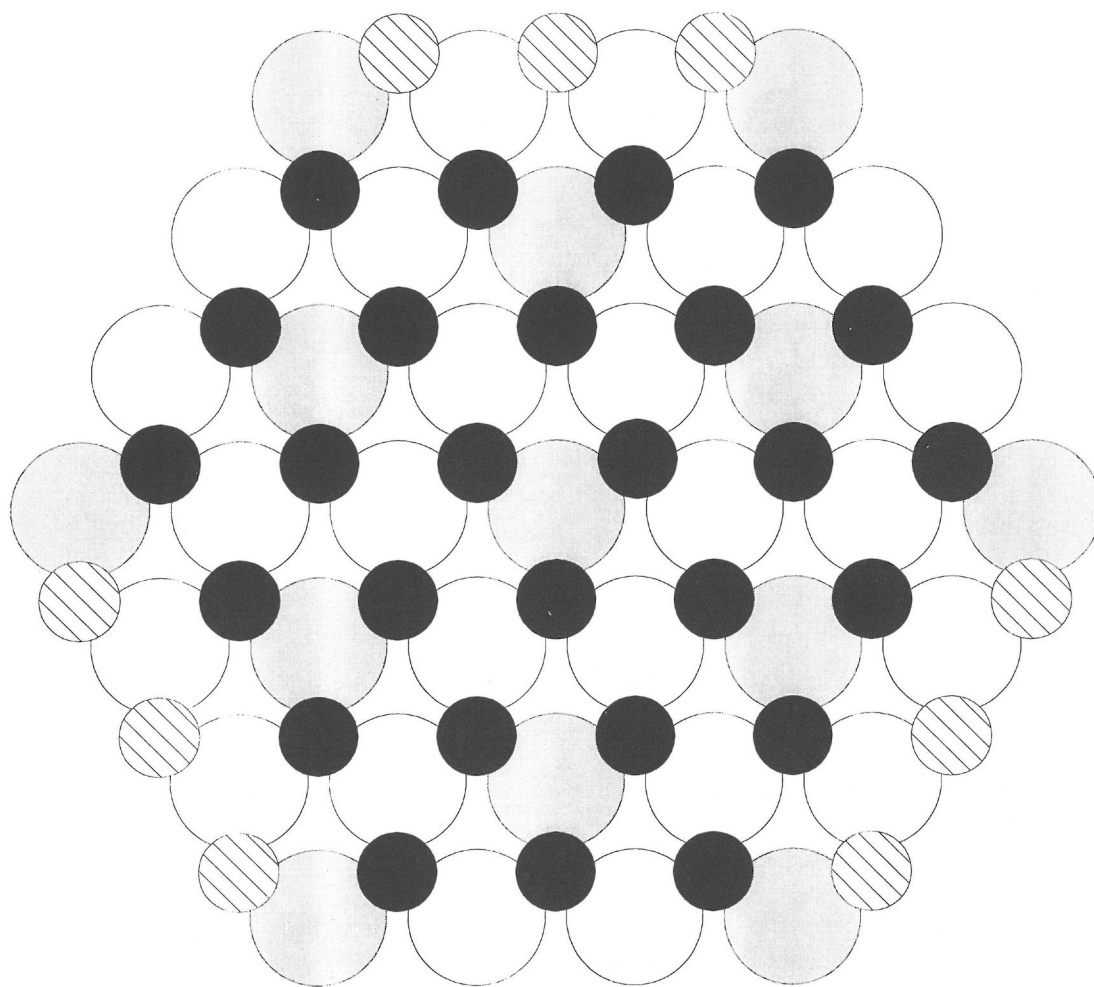


Figure 9. Partial octahedral layer in talc.

On the octahedral template put an oxygen or hydroxyl in each position, as shown. Glue on the Mg^{2+} ions to hold the layer together. Nine Mg^{2+} ions (hatch pattern) on two edges will have to wait until the glue is dry.

When the glue is dry, flip this layer over onto a flat surface. Glue the remaining nine Mg^{2+} ions into place as shown.

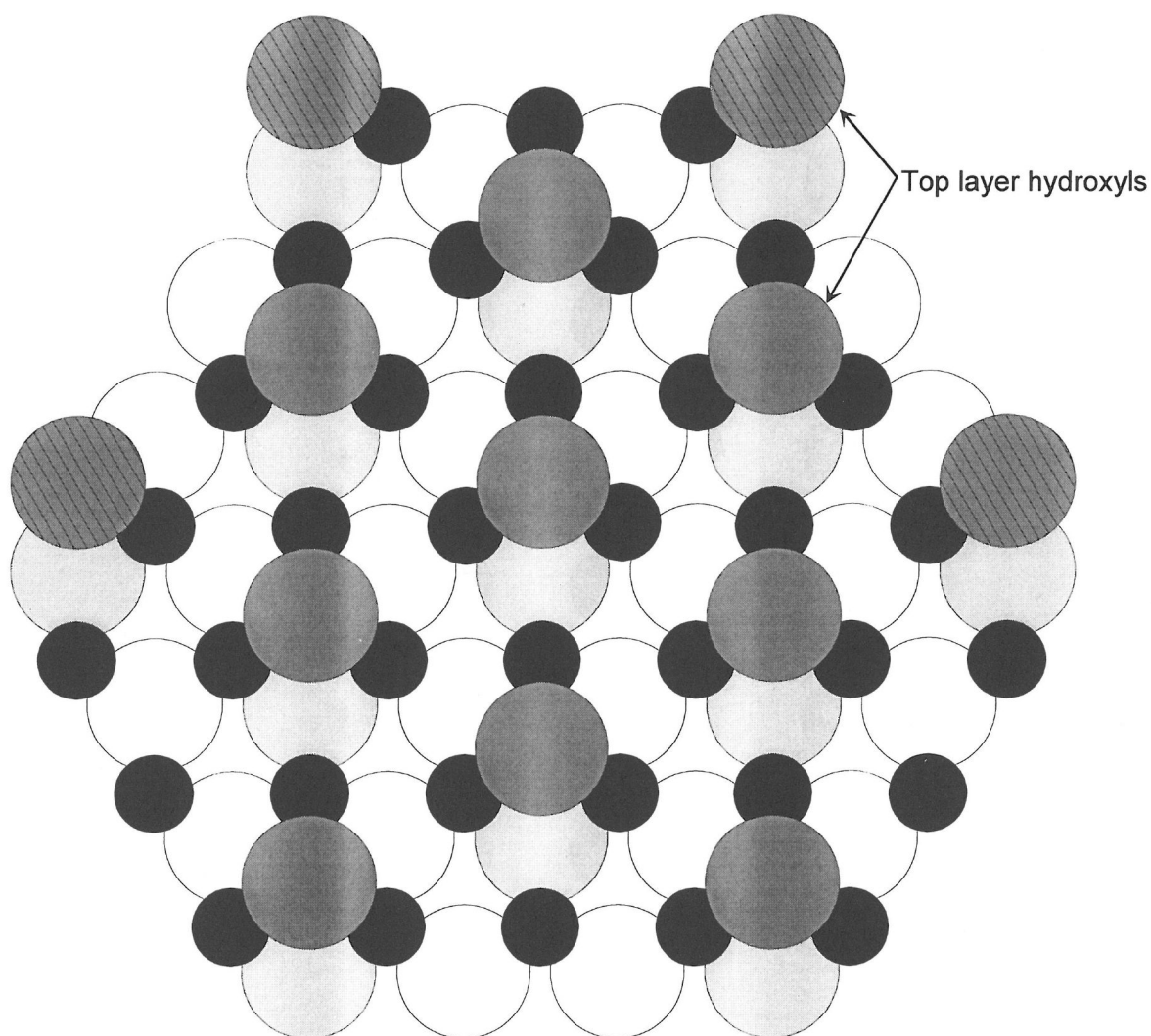


Figure 10. Top layer hydroxyls for the octahedral layer in talc.

Start with the partial octahedral layer from Figure 9. Nine top layer hydroxyls fit nicely between the triangles of Mg^{2+} ions without rolling away. These make the hydroxyl pairs. Glue these in place. Four hydroxyls (hatch pattern) must wait until the glue on the other nine is dry.

When the glue is dry, flip the layer over onto an octahedral template. Fit the remaining four hydroxyls in place and glue them. You may have to support each with a bit of paper to make sure they touch and glue firmly to the adjacent atoms.

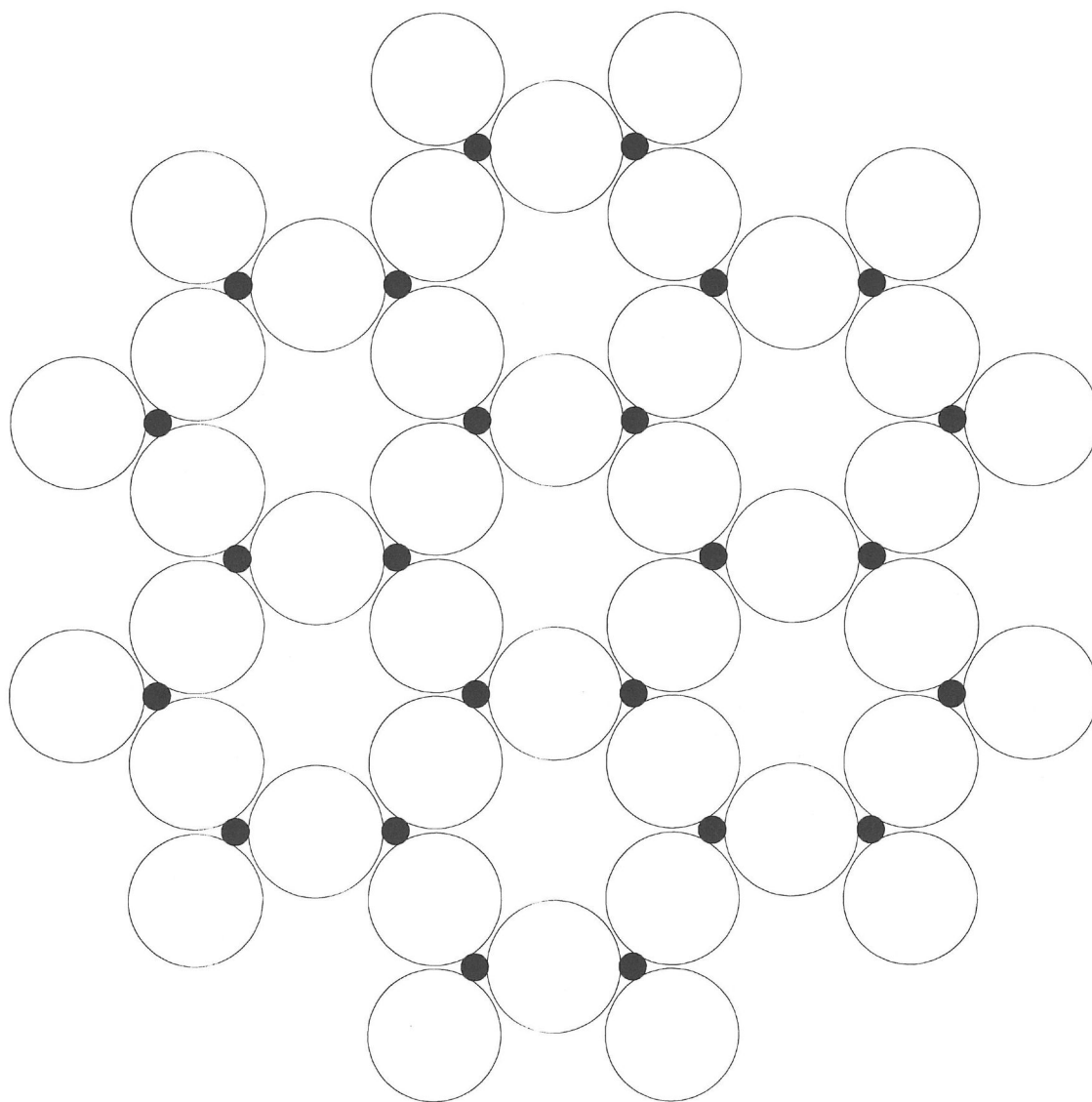


Figure 11. Incomplete tetrahedral layer for talc.

On a tetrahedral template put an oxygen in each position, gluing them together as you go. Put a silicon over each oxygen triangle, but do not glue them. These silicons will be covered by oxygens in the octahedral layer from Figure 10, as shown in Figure 12.

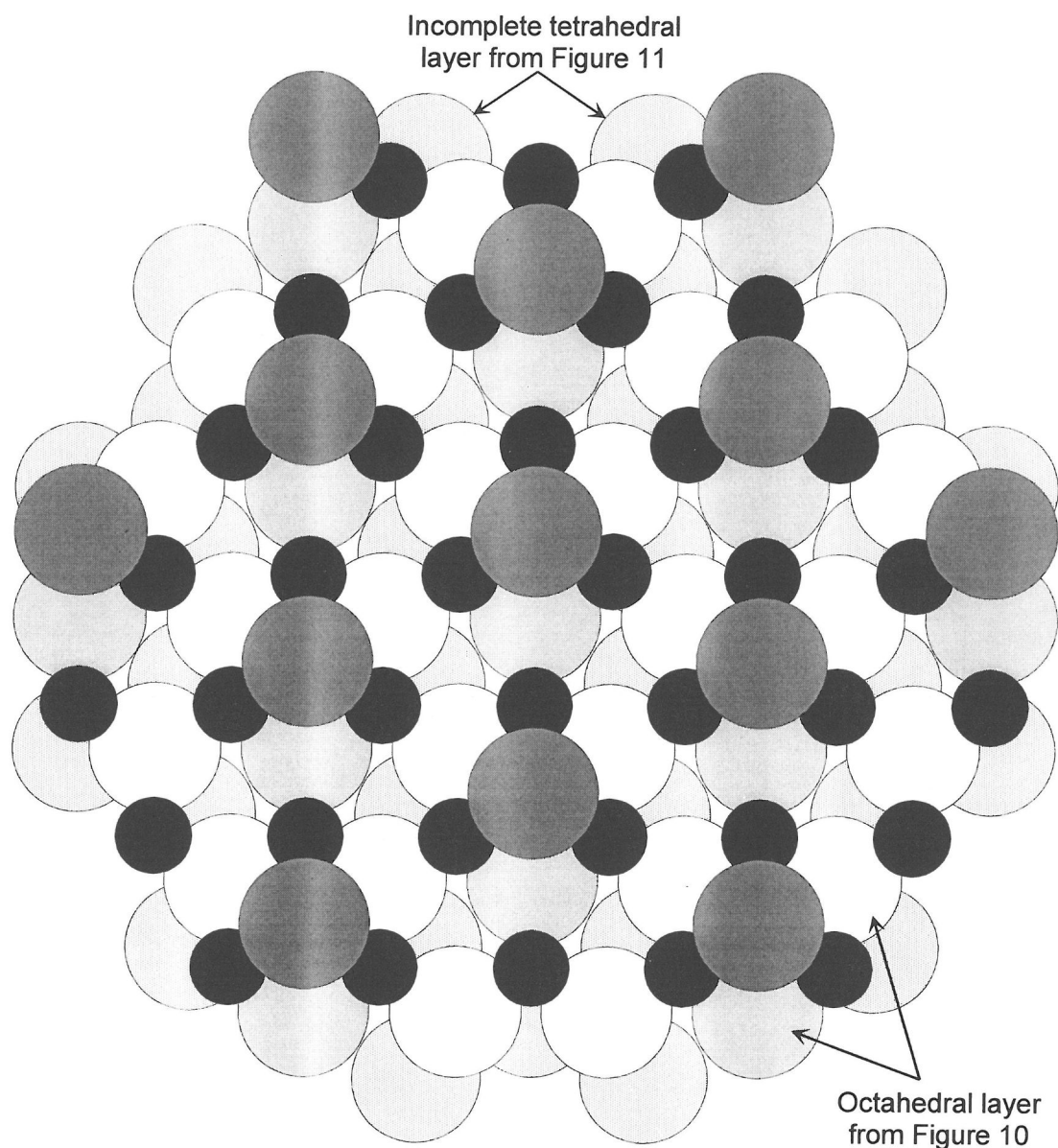


Figure 12. Gluing the incomplete tetrahedral layer to the octahedral layer for talc.

Take the incomplete tetrahedral layer from Figure 11 (stippled above) and on top of it lay the octahedral layer from Figure 10. Orient the octahedral layer so that its oxygens rest exactly over all of the silicons on the incomplete tetrahedral layer. Once you see how the octahedral layer fits, remove the octahedral layer, put glue on appropriate spots on the incomplete tetrahedral layer oxygens, and replace the octahedral layer. Let the glue dry and this structure is finished.

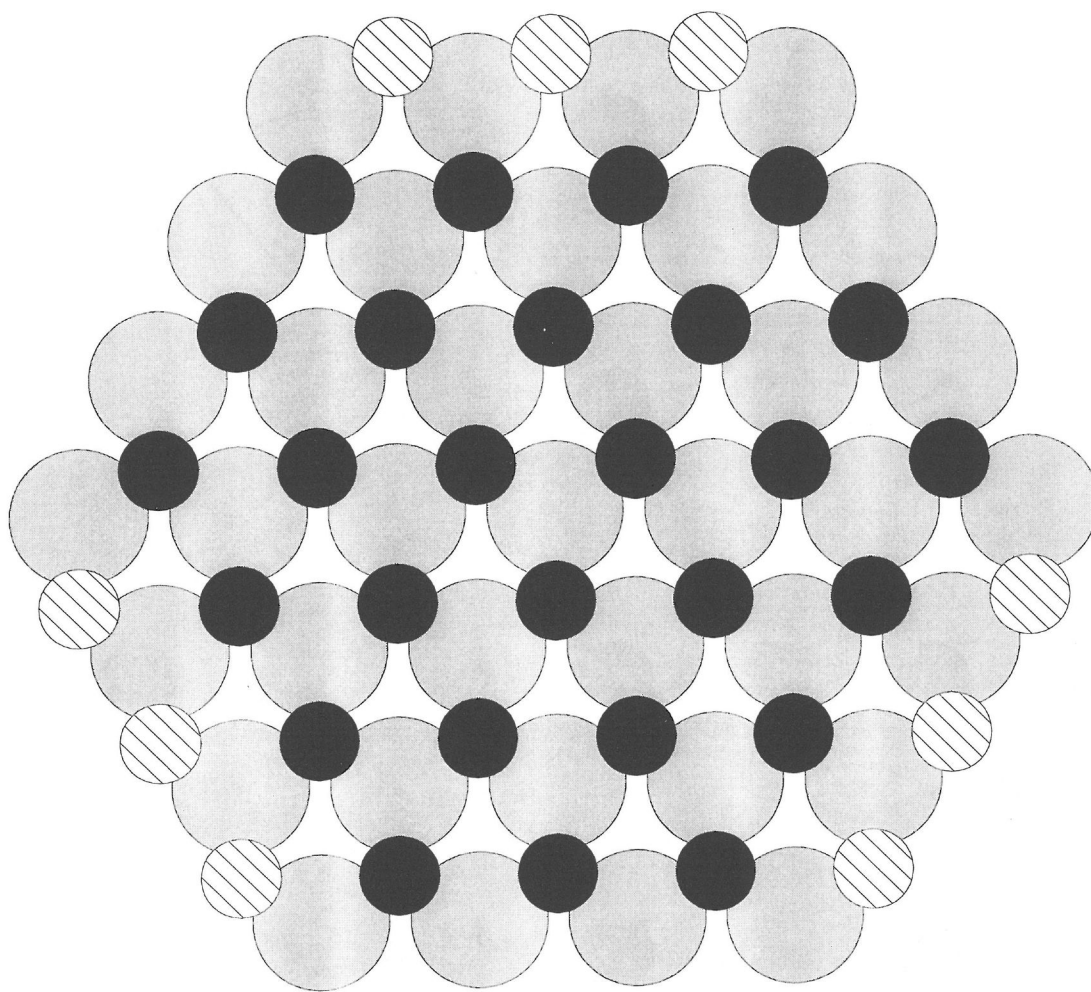


Figure 13. Bottom layer hydroxyls for the octahedral layer of serpentine and brucite.

On an octahedral template put an hydroxyl in each position. Then glue on Mg^{2+} ions to hold the layer together. Nine of the Mg^{2+} ions on the edges (hatched pattern) will have to wait until this layer dries.

When dry, flip this layer over onto a flat surface. Then glue on the remaining nine Mg^{2+} ions in place.

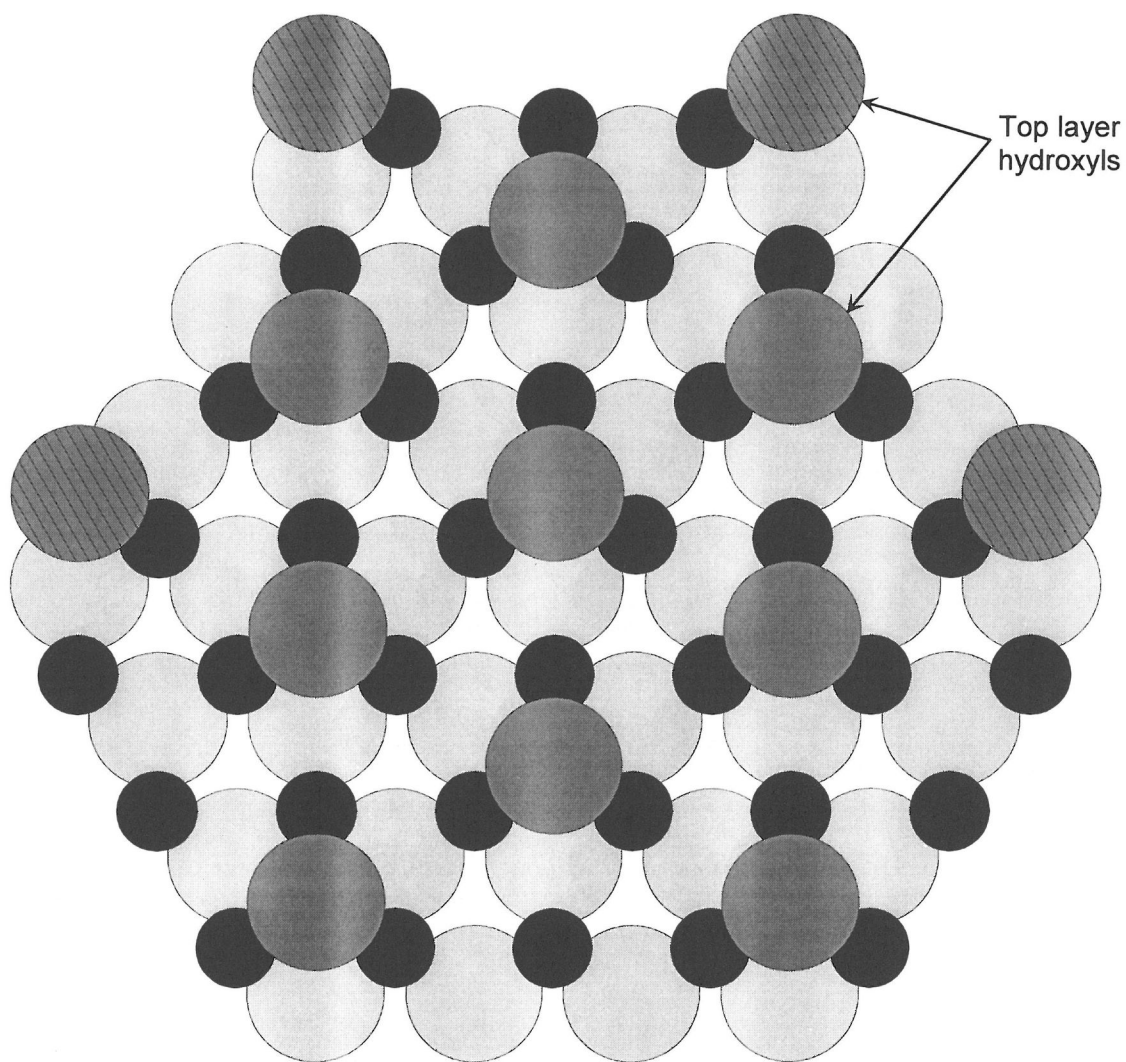


Figure 14 Top layer hydroxyls for the octahedral layer in serpentine.

Take the octahedral layer from Figure 13. Nine hydroxyls fit nicely between the triangles of Mg^{2+} ions without rolling away. Glue these in place. Four hydroxyls (hatch pattern) must wait until the glue on the other nine is dry.

When the glue is dry, flip the layer over onto an octahedral template. Fit the remaining four hydroxyls into place and glue them. You may have to support each with a bit of paper to make sure that they touch and glue firmly to adjacent atoms.

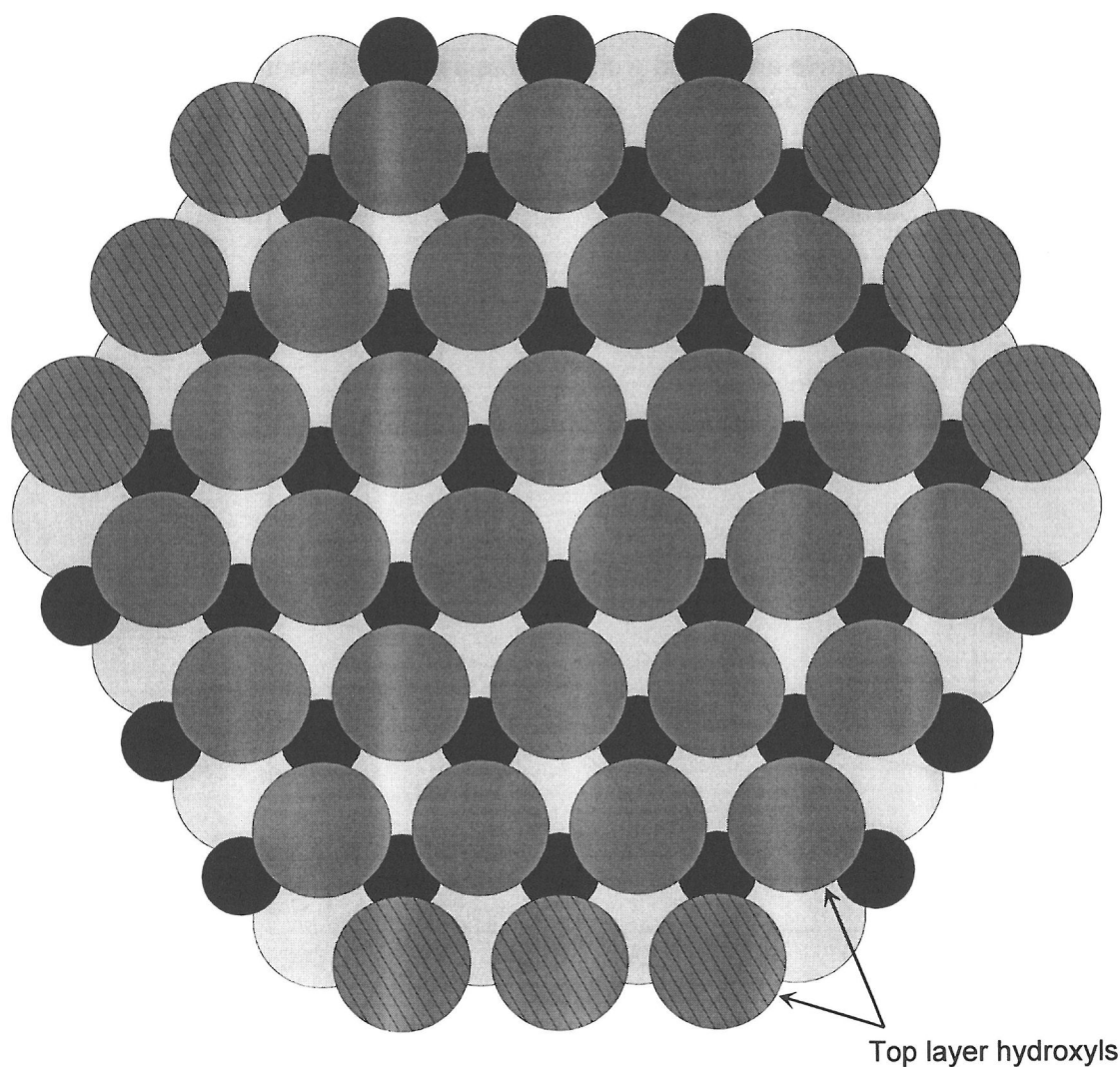


Figure 15. Top layer hydroxyls in the octahedral brucite layer.

Take the octahedral layer from Figure 13. Most of the top layer hydroxyls fit nicely between Mg^{2+} triangles without rolling away. Glue these in place. Nine hydroxyls (hatch pattern) on the edges will have to wait until the glue is dry.

When the glue is dry, flip the octahedral sheet upside down onto a flat surface. Glue the remaining nine hydroxyls into place as shown. When the glue is dry, this structure is done.

Figure 16. Phase diagram showing the P-T stability fields of the silica polymorphs. The stability fields of α and β tridymite and α and β cristobalite are not differentiated. Modified after Klein and Hurlbut (1993, p. 527).

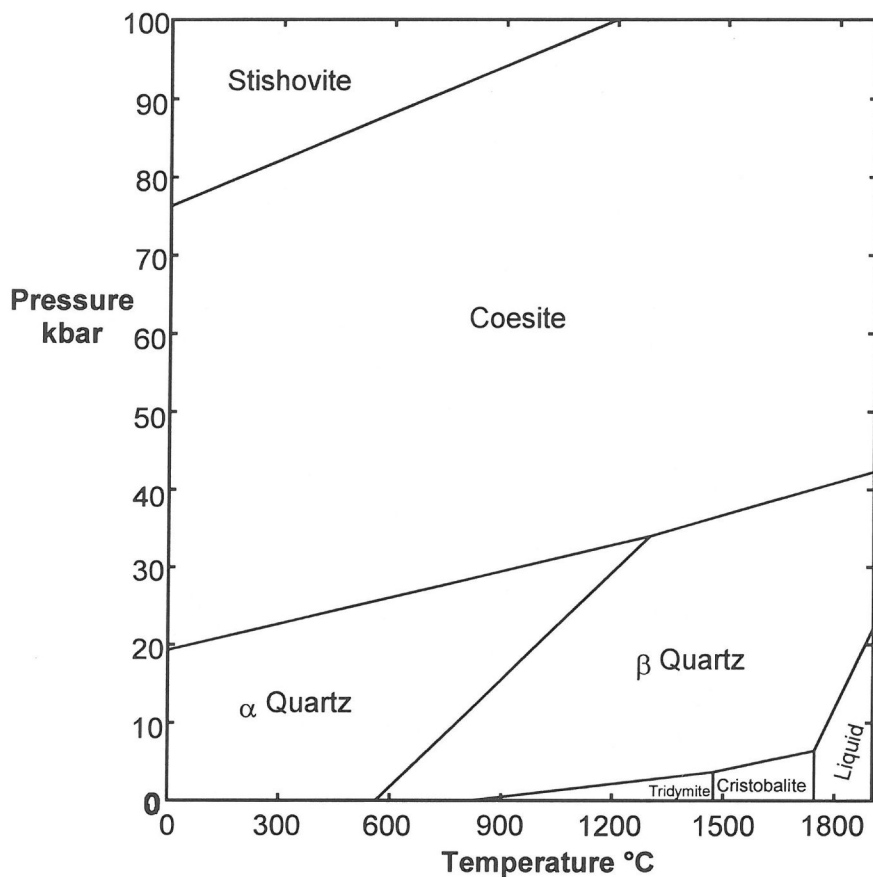
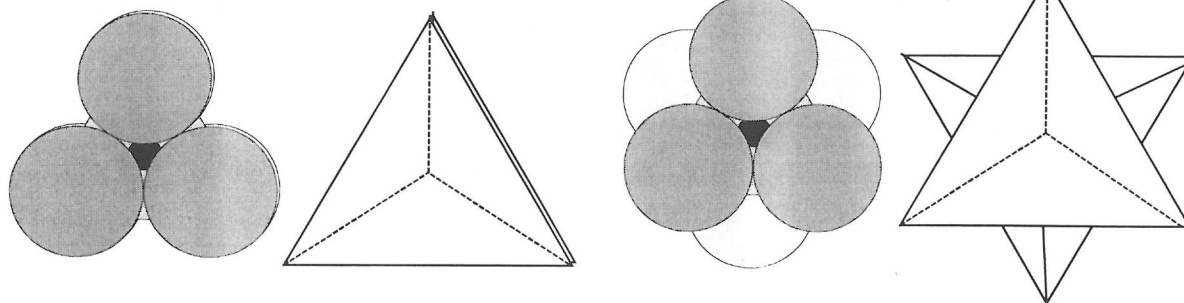


Figure 17 Views of adjacent corner-sharing silicon-oxygen tetrahedra in tridymite (A) and cristobalite (B) as viewed perpendicular to the construction sheets. This view is down the c axis in tridymite, and down one of the $\bar{3}$ axes in cristobalite. In tridymite, overlying tetrahedra are oriented the same way as, and so exactly cover, underlying tetrahedra. In cristobalite, overlying tetrahedra are rotated 60° with respect to underlying tetrahedra, and so are partly in view.

A. Tridymite: underlying tetrahedron is hidden.

B. Cristobalite: underlying tetrahedron is visible.



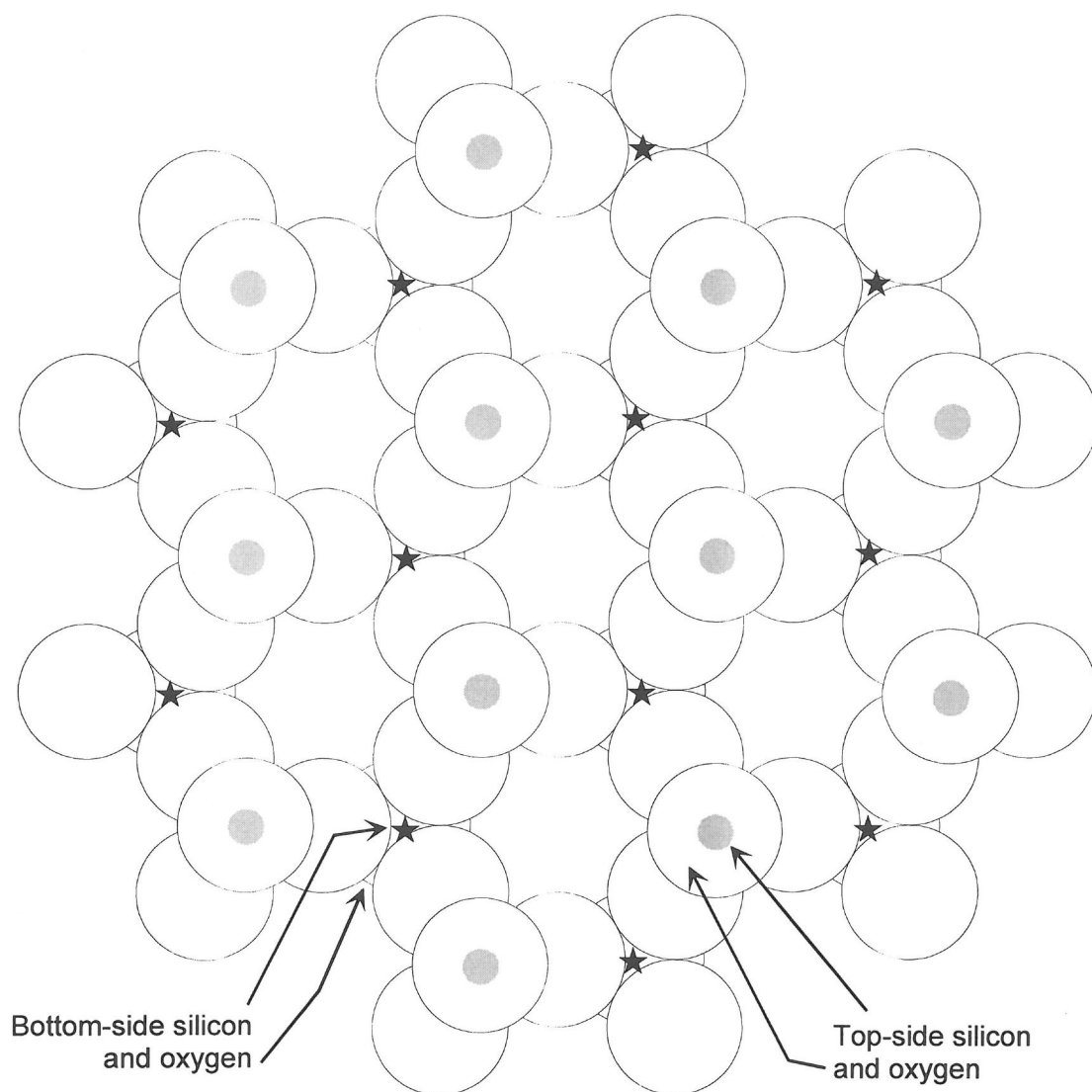


Figure 18. Tridymite layers 1 and 3. Make 2.

The whole model takes 174 O and 72 Si.

On a tetrahedral template put one layer of oxygens in each position, gluing them together as you go. Then put a top-side silicon over half of the oxygen triangles, as shown, and glue an oxygen above each silicon. Let this structure dry.

When dry, remove the structure from the template and flip it over onto a flat surface. Then put a bottom-side silicon over the other half of the oxygen triangles, and glue an oxygen above each of these silicons.

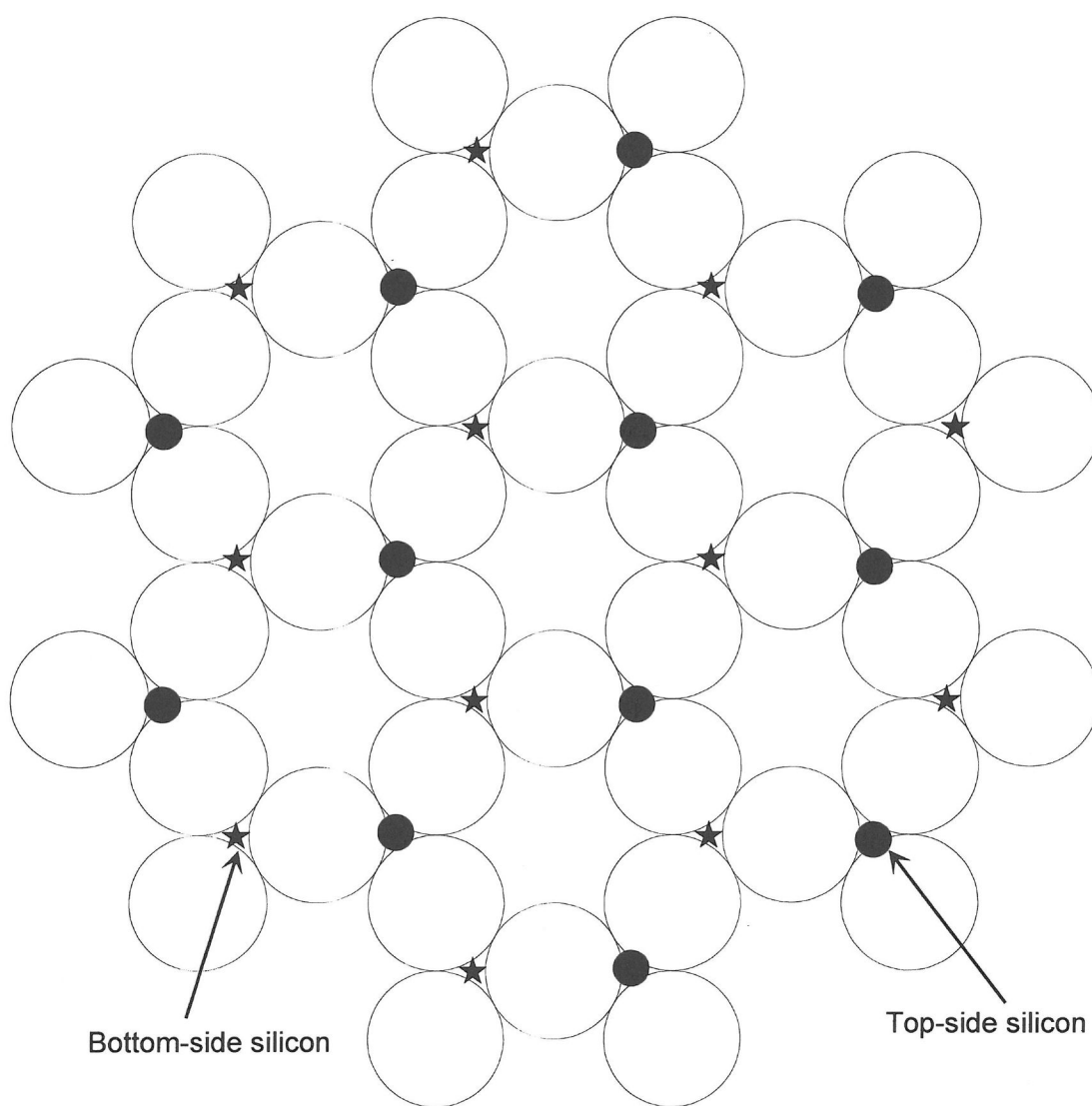


Figure 19. Tridymite layer 2 and final assembly. Make 1.

On a tetrahedral template put an oxygen in each position, gluing them together as you go. Put a top-side silicon in half the oxygen triangles, as shown, but do not glue them.

Final Assembly

Take layer 1 from Figure 18 and glue it onto layer 2, above, so the bottom-side oxygens on layer 1 rest on top of the top-side silicons on layer 2. Wait for the glue to dry.

When dry, flip this assembly over and put bottom side silicons into the rest of the layer 2 oxygen triangles. Flip layer 3 over and glue it onto layer 2 so that, the apex oxygens cover the bottom side silicons. Tetrahedra in successive layers should lie directly above one another, hiding tetrahedra lying below and to make hexagonal channels parallel to c.

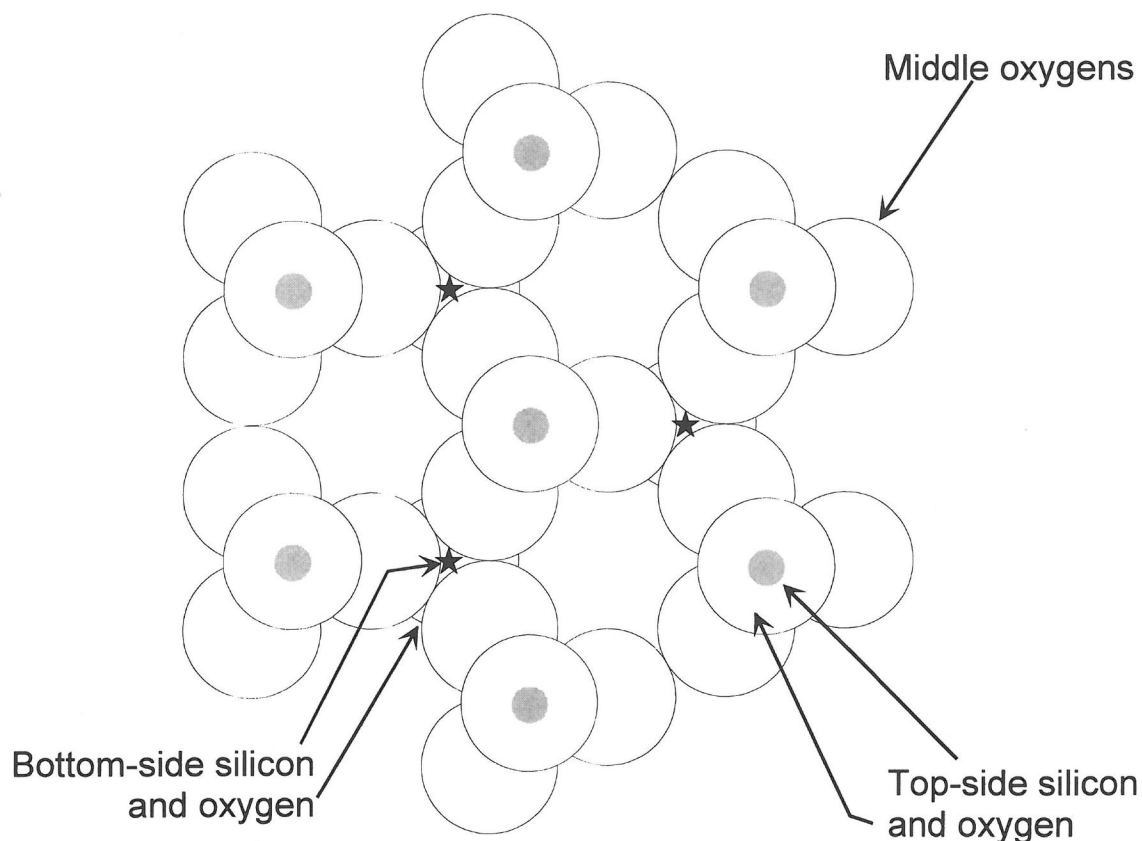


Figure 20. Cristobalite layer 1.

The whole model takes 164 O and 41 Si

On a tetrahedral template put an oxygen in each middle oxygen position shown, gluing them together as you go. Put a top-side silicon in seven of the oxygen triangles, as shown, and glue oxygens over the silicons. Wait for the glue to dry.

When dry, turn this layer over and put three bottom side silicons into the remaining oxygen triangles, and glue on the three bottom side oxygens.

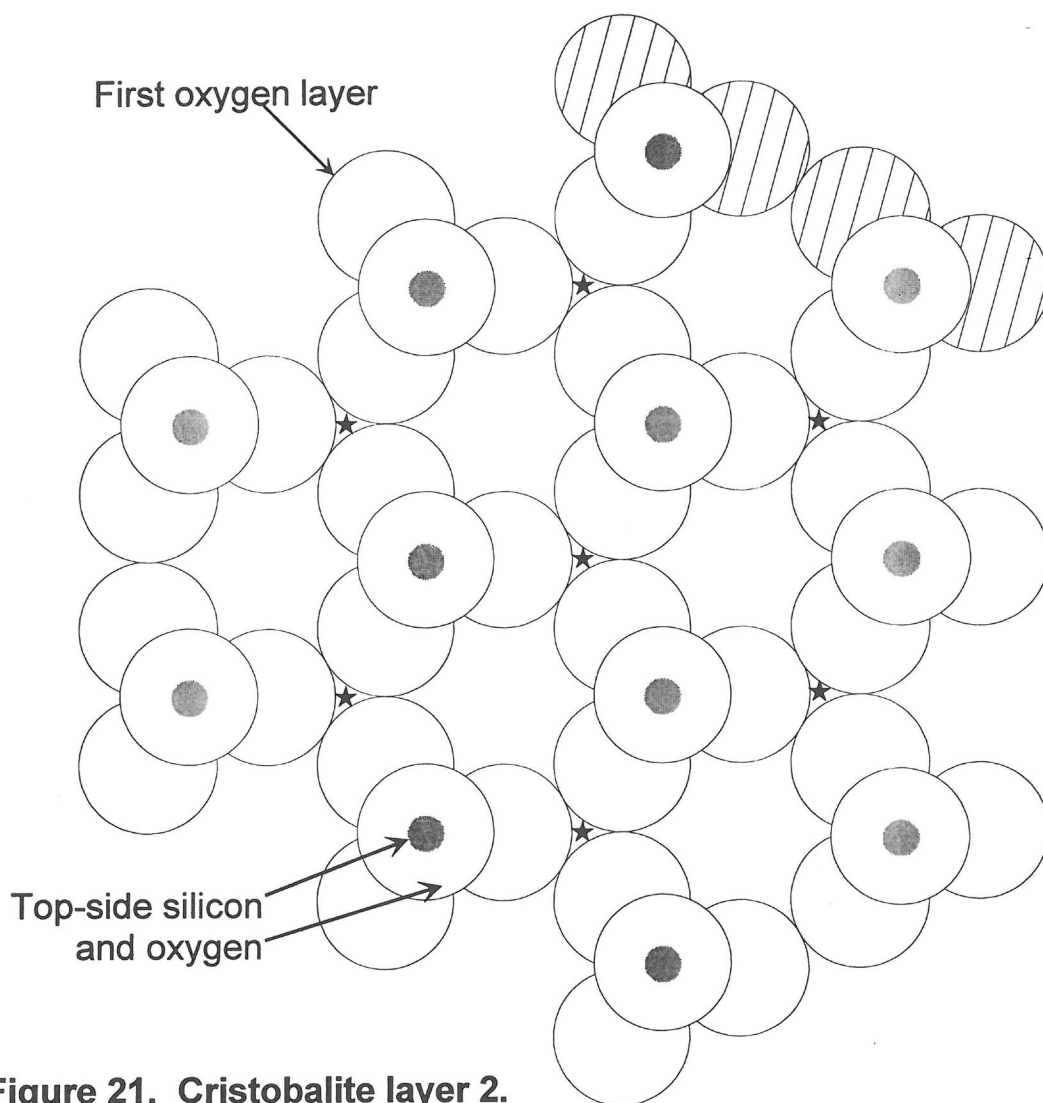


Figure 21. Cristobalite layer 2.

On a tetrahedral template make the first oxygen layer by putting oxygens in the positions shown, except those with the hatched pattern, gluing them together as you go. Four oxygens (hatched pattern) will not fit on a standard template, so on another template glue 4 oxygens in a row. Wait for the glue to dry.

When dry, remove the two assemblies from their templates and put them on a flat surface. Glue the four oxygen assembly onto the larger assembly as shown. Wait for the glue to dry.

When dry, put a top-side silicon over half of the oxygen triangles, as shown, and glue an oxygen above each silicon.

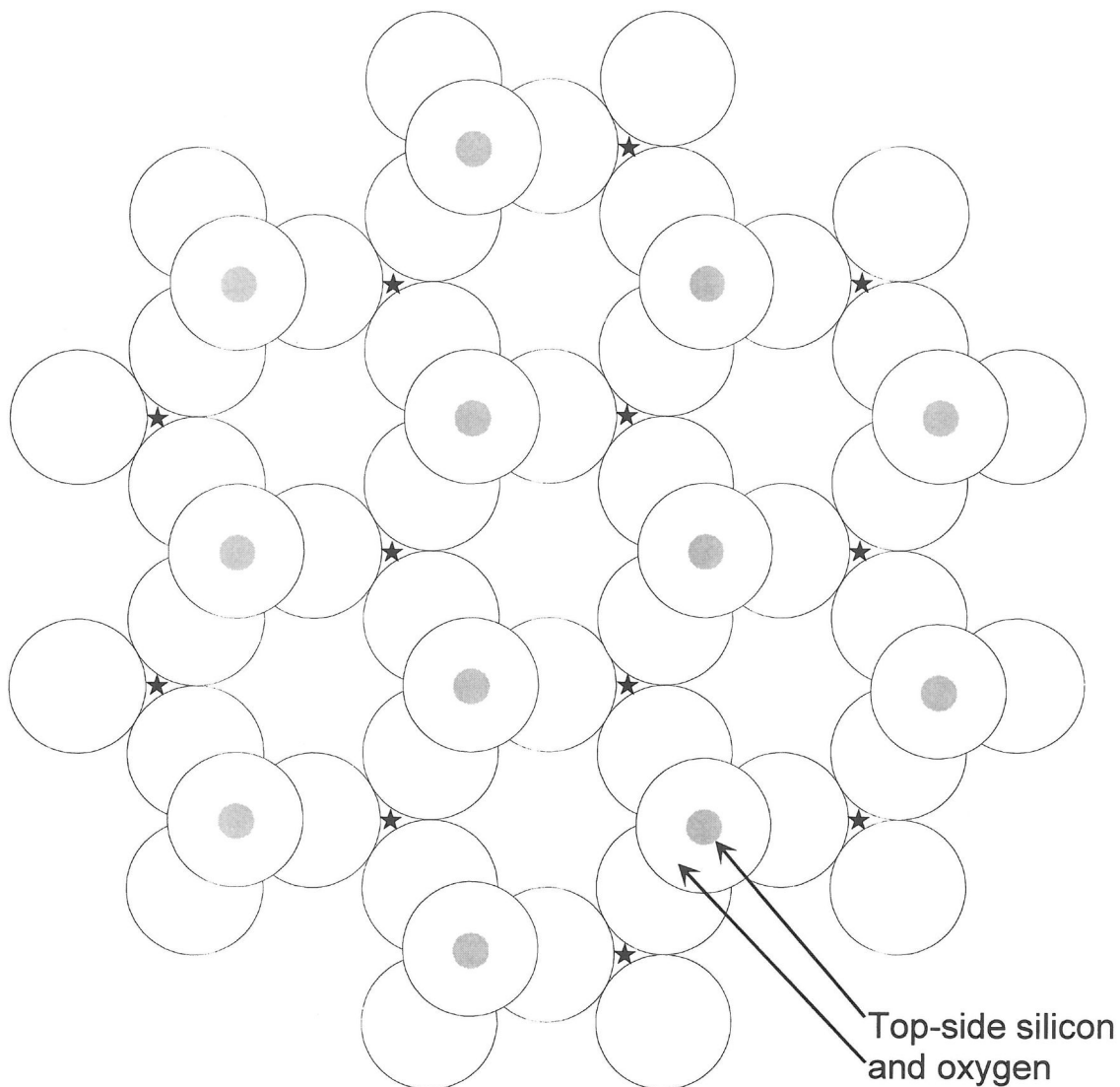


Figure 22. Cristobalite layer 3.

On a tetrahedral template put one layer of oxygens in each position on the template as shown, gluing them together as you go. Then put a top-side silicon over half of the oxygen triangles, as shown, and glue an oxygen above each silicon.

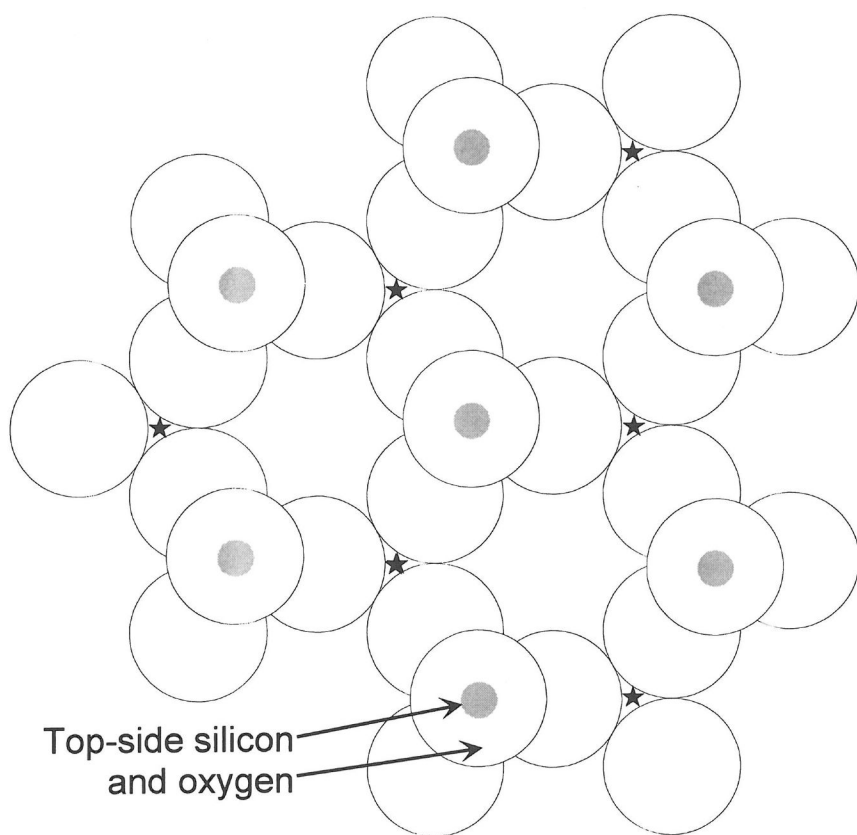


Figure 23. Cristobalite layer 4.

On a tetrahedral template put an oxygen in each position shown, gluing them together as you go. Put a top-side silicon in seven of the oxygen triangles, as shown, and glue oxygens over the silicons.

Final assembly

When the layers are dry, turn layer 4 upside down. Put silicons into the open oxygen triangles as indicated by the stars in Figure 23. Turn layer 3 upside down and glue it so that its apex oxygens exactly cover the loose silicons on layer 4. Then put silicons into the open oxygen triangles in layer 3, as indicated by the stars in Figure 22. Turn layer 2 upside down and glue it so that the oxygens exactly cover the loose silicons on layer 3. Lastly, put the 7 silicons onto the open oxygen triangles in layer 2, as shown by the stars in Figure 21. Turn layer 1 upside down and glue it so that the loose silicons on layer 2 are covered. When the glue is dry, the cristobalite model is finished.

DIRECTED-DISCOVERY OF CRYSTAL STRUCTURES USING BALL AND STICK MODELS

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INTRODUCTION

Understanding relationships in three dimensional objects, whether crystal structures or the architecture of mountain belts, presents formidable barriers to understanding for many students in the geosciences. Students may have a difficult time mastering concepts of crystallography and crystal chemistry because a) it is typically their first formal encounter with 3-D visualization, b) the crystal structures may appear to be too complex and abstract, and thus overwhelming for many students, and c) instruction on crystal structures may be out of context with respect to other course content or future geologic applications. Two-dimensional representations of crystal structures presented as line drawings or perspective diagrams in textbooks are inadequate to convey fundamental 3-D relations to students. Use of computer models (e.g., SHAPE and ATOMS, see contributions of Brock and Velbel, this volume) and building crystal models (see Hollocher, this volume) provide significant improvements in instruction on crystal structures. Although computer simulations are useful for many crystallographic representations, it is also necessary to provide students with opportunities to work with physical materials. This exercise provides a series of activities in which students manipulate ball and stick models to discover for themselves the underlying relationships of crystal structures and the principles of crystallography and crystal chemistry.

One of the key recommendations of *Project 2061 Science for All Americans* (AAAS, 1989) is "start with the concrete and work towards the abstract". In this regard, ball and stick models are great materials for students to explore as they first encounter the internal arrangement of atoms in minerals. The increased emphasis on "hands-on", and more importantly, "discovery-based" learning experiences is effectively implemented as students manipulate ball and stick models. But open-ended discovery, i.e. turning the students loose without specific instructions or expectations of outcomes, may prove to be very frustrating to students. They may not know where to start, what to look for, or how to interpret the various relationships. I advocate a "directed-discovery" approach in which students are given specific instructions on where to look for relationships, but they must find these relationships for themselves. It is also important that directions be given to a) place the observations in appropriate contexts with respect to fundamental chemical and physical principles, and b) make connections to other bodies of knowledge that have already been covered, or in anticipation of new material that will be covered, in the course.

In this series of exercises, a kind of reductionist approach is used to direct the students attention to specific characteristics of a variety of ball and stick models. Through a series of leading questions, students must focus on specific relationships and must rationalize these relationships according to the fundamental principles of crystal chemistry and crystallography. In this way, students will simulate and replicate the kinds of questions we would normally ask in our professional careers as mineralogists. This approach also addresses other major recommendations from *Project 2061*: start with questions about nature, and concentrate on the collection and use of evidence. Other questions ask students to make connections to basic chemistry (e.g. bond types, relative strength of bonds, bond angles), determinative mineralogy (most likely place to develop cleavage), analytical techniques (e.g. preferred orientations for X-ray analysis), and so on. The

final reflection questions will allow students to "discover" Pauling's Rules, a much more effective learning strategy than simple memorization of these rules (commonly with little or no understanding on the part of the students).

The ball and stick models may be used in a number of different instructional modes. It may be necessary for you to provide a demonstration to the class, pointing out the relationships that can be seen in a given model, showing how to look at the crystal in different orientations, identifying the location of close packed layers of oxygen, pointing out similarities among sites with balls of the same color, noting the presence of voids in the structures, etc. It may be appropriate to put the models out for self-paced learning exercises, allowing the students to spend as much time as they need on a given model before they move on to the next. I have found that interactive learning strategies (see Srogi and Baloché, this volume) are particularly effective. Try the jigsaw technique by assigning small groups of students to be the "experts" on a given crystal structure, and then reassign students to new groups to teach each other about the important relationships for each assigned structure. Have the "experts" compare similarities among different structures such as different types of tectosilicates, or between pyroxenes, amphiboles, and micas. Outcomes could be written short answers to the questions, longer integrative writing assignments, or verbal articulation of answers to peers or instructors. If you have a collection of ball and stick models, refer to these throughout the course to make connections between different content areas in reference to determinative properties of minerals, to introduce new mineral groups in hand sample, to introduce the techniques of X-ray diffraction, and to explain why different minerals give different powder (or precession) patterns, etc.

The ball and stick models described below are common structures or rock-forming minerals that I happen to have in my collection. These models are expensive, and you may have access to only a few. You may find that some of these models are stashed away in other departments (chemistry, physics, materials sciences; it's worth looking around). In any case, in-depth exploration of any 3-D crystal models through directed discovery will be a beneficial learning experience for students. Amend these questions to meet your own instructional needs, or use these questions as models for developing similar exercises for other crystal models.

ASSIGNMENT

For each of the crystal models, identify the features outlined in the following questions. A starting orientation is suggested for each model, but you should also physically rotate all the models to look at them from many directions. Pay special attention to the different types of atoms represented in each structure (different colored balls). Note what other atoms are "in the neighborhood" and how many nearest neighbor atoms are in the structure. Check to see if each cation is in an electronically neutral environment (or nearly so). Note the bond lengths and bond angles. For minerals with oxygen as the dominant anion look for close packed arrays of oxygen. Look for coordination polyhedra and ways in which these polyhedra come together to form the overall structure. Look for regular repetitions of atoms or groups of atoms (i.e. symmetry). All references to figures and pages numbers are to Klein and Hurlbut (1993) *Manual of Mineralogy*, John Wiley & Sons. Use this text as a reference to help with your understanding of the crystal structures. For more detailed descriptions of crystal structures, consult the Reviews in Mineralogy series, published by the Mineralogical Society of America. The models used are from Klinger Educational Products.

Magnesium metal (see Fig. 10.1, p. 337)

- All of the atoms have the same atomic radius. What is the coordination number of any Mg atom in this structure?
- Stand the model on the three metal legs. What is the stacking arrangement of the layers (ABCABC, or ABAB)? Is this a CCP or HCP structure?
- Look directly down on the model in the above orientation. Rotate the model 120° . Do similar atoms occupy exactly the same positions, or are they in a different arrangement? Try the same with a 90° and 180° rotation.

Graphite, C, (see Fig. 10.8, p. 344)

- What is the coordination number for each C atom in the horizontal planes?
- What kind of orbitals does C have in this structure?
- What type of bonds occur within the layers, and between the layers?
- What is the bond angle between C atoms in the horizontal planes?
- Describe the geometrical arrangements of C atoms that repeat in similar patterns in the horizontal planes. How many atoms occur in these groups?
- Look directly down on the horizontal plane. Rotate the structure until similar atoms occupy identical positions. How many degrees of rotation are needed to repeat this structure? Note the relationship between bond angle and atomic positions.
- Look at the model from a side view. Now flip it over, top to bottom (180°). Do the atomic positions exactly repeat themselves?
- Describe any planes (horizontal or vertical) that might pass through the crystal such that atomic positions on one side of the plane are exactly the same as atomic positions on the other side.
- How many cleavages would you expect in graphite? What is the hardness of graphite? What controls this physical property?

Diamond, C, (see Fig. 10.8, p. 344)

- What is the coordination number for each C atom?
- What is the shape of the polyhedron that forms if all of the nearest neighbor C atoms are connected?
- What type of orbitals does a C atom have in this type of structure?
- What type of bonds occur in diamond? What are the bond angles?
- What is the relationship between bond type and hardness? Bond angle and cleavage? How many cleavage planes would you expect in diamond. Try to locate these on the structure.
- Stand the model on its legs and look directly down. Inside the structure there is the outline of the cubic unit cell, outlined by heavier metal rods. Look down the long, body diagonal of the cube. Rotate 120° and see if the atoms occupy the same exact positions. Try this for the other long body diagonals of the unit cell cube.
- If you find a flat, square face of the unit cell cube, you might expect that a 90° rotation will repeat the atomic arrangement. It does not! Explain why. (Hint: look up the meaning of 4-fold screw axis.)
- How can C occur in two different types of crystal structures? (Hint: look up the meaning of polymorph.)

Wurtzite, ZnS , Zn=silver, S=yellow (see Fig. 10.23, p. 357)

- What is the coordination number for Zn? For S?
- The Zn and S atoms are each in a close packed structure. What kind?
- What type of bond forms between the S and the Zn?
- Look down onto the central S atom. What is the symmetry (e.g. How many degree rotation is necessary to replicate the same atomic positions)?

Halite, NaCl , Na=silver, Cl=red (see Fig. 4.42, p. 211; Fig. 11.37, p. 398)

- What is the coordination number for Na?
- What type of polyhedron forms around the cations?
- What type of bond occurs in NaCl? Is it a directional bond?
- How many cleavages occur in NaCl? What is the angle between them?
- Look at a single row of atoms that are perpendicular to one of the flat faces. What is the symmetry in this direction?
- Look at the body diagonal (i.e. stand the model on one of the corners). Look down this diagonal and determine the symmetry. How many identical rotation axes occur in this structure?
- Identify any planes in the structure that exactly replicate positions of the same kinds of atoms equidistant on both sides of the plane. How many sets of planes occur in this structure (these will have the same orientation); what is the angular relation between different sets of planes?

Cesium Chloride, CsCl , Cs=silver, Cl=red (see Fig. 4.43, p. 211)

- What is the coordination number of Cs?
- What is the polyhedron that forms around Cs?
- Compare the structures of NaCl and CsCl. Why are they different? (Hint: use the periodic table.)
- Which is more soluble, NaCl or CsCl, and why? Which element, Na or Cs, will most readily fit into mineral structures, which will be excluded during a crystallization sequence (i.e. it will be concentrated in a magma) and why?

Calcite, CaCO_3 , Ca=silver, C=black, O=red (see Fig. 12.2, page 404)

- What is the coordination number of C? (see Fig. 4.22 G, p. 194)
- What is the radius ratio (cation/anion) for carbonates?
- Note that the calcite structure contains alternating planes of carbonate complexes and Ca atoms.
- Look down the axis of the rhomb (body diagonal). What is the symmetry? Is this consistent with the bond angles in the carbonate complexes?

Spinel, MgAl_2O_4 , Mg=wood, Al=silver, O=red (see Fig. 11.5, p. 375; Fig. 11.6, p. 376; Fig. 4.48, p. 213-214)

- Stand the model on the long diagonal, with a silver ball on top. Note the horizontal planes of close packed oxygen. Is this HCP or CCP?
- What is the coordination number for Mg? For Al?
- Note the numerous "voids" in the structure. Why are they present? What percentage of the possible tetrahedral sites, and what percentage of the possible octahedral sites are filled?

- d) Note the overall cubic form of this structure. Look down any of the long, body diagonals of the structure and you will see that these are 3-fold axes. How many 3-fold axes are present? There are more symmetry elements present in this structure but they are difficult to find because they are complicated combinations of glide planes and screw axes.

Olivine, $(\text{Mg,Fe})_2\text{SiO}_4$, O= red, Mg,Fe=silver, Si=black; (see Fig. 13.4, p. 445)

- What is the coordination number of Si, and Mg?
- What is the relationship of the Si tetrahedra? Are they somehow connected to each other or are they independent of each other? Hint: look at the corners of the Si polyhedra and see what they are connected to in the structure.
- What is the relationship of the Si and Mg polyhedra? Are they connected to each other? If so, how are the Si and Mg polyhedra connected (what structural components do they share)?
- Orient the model so that the shortest dimension is vertical, and the longest axis is left and right. From the side, note the layers of O atoms. From the top, note the close packed array of O. Can you predict the position of the next series of O atoms as this structure is extended into space (i.e. during crystal growth)? Rotate the crystal on the table (i.e. look from the side) until rows of Mg atoms are perfectly aligned. This same procedure of rotating crystals into preferred orientations is essentially what is done during single crystal X-ray analysis to determine crystallographic parameters such as measurement of unit cell dimensions and interaxial angles.
- Compare the olivine structure to the spinel structure. Both have model formulas of XY_2O_4 (i.e. one tetrahedral site and two octahedral sites). Which mineral appears to have greater symmetry? Which mineral appears to have a greater density? Olivine and spinel minerals are both found in the mantle. Which structure will be favored by very high pressures, and why?

Diopside $\text{CaMgSi}_2\text{O}_6$; O=red, Si=black, Mg=silver, Ca=gold; see Fig. 13.48 p. 477

- Orient the model so that the shortest dimension is front to back and layers of oxygen roughly alternate with layers of Ca and Mg. What is the coordination of Si, Mg, and Ca?
- Focus on the Si tetrahedra and their arrangement in this structure. Diopside is an "inosilicate" or "single chain silicate". Look carefully and find the chain of Si tetrahedra. Within a given chain, how are the Si tetrahedra connected to each other? The oxygen atom that connects adjacent tetrahedra along the chain are called bridging oxygens. Look at a chain internal to the crystal, and note that 3 of the oxygen in each polyhedron are roughly in the same plane, and that a fourth oxygen in each tetrahedron "points" either up or down. What is this oxygen connected to? Are any of the chains of Si tetrahedra directly connected to any other chain?
- Compare this 3-D view of diopside with the perspective drawing in figure 13.49 (p. 477). This view is looking down the c-crystallographic axis. Note that when viewed down the length of the chain, alternating Si tetrahedra are slightly offset. Each chain of tetrahedra will be connected to an adjacent octahedral layer by the fourth oxygen (noted above), and this octahedral strip will also be connected to a second tetrahedral chain on its other side. This produces the T-O-T structure of alternating tetrahedral-octahedral-tetrahedral layers, commonly referred to as the "I-beam" structure. Make sure that you can identify this basic structure in the ball and stick model.
- Compare the directions of the cleavage planes illustrated in figure 13.49 and see if you can find their location on the model structure. What are the relative bond strengths within the Si tetrahedra compared with bonds involving octahedral sites?
- Turn the model 90° (looking at the smallest face). This view shows the c-axis (left and right) and the a-axis (near vertical). Note that the structure appears to be "inclined" or tilted to one side. Imagine a line that connects identical atoms on the top plane and bottom plane (e.g.

identical Ca or Mg atoms) this is the a-axis, and a line parallel to the chains of Si tetrahedra is the c-axis. The angle between these two lines is the β angle (the angle between a and c axes) which is $> 90^\circ$ for monoclinic crystals such as diopside.

Tremolite $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ O=red, Si=black, Mg=silver, Ca=gold, OH=green (see Fig. 13.66 and 13.67, p. 490)

- Orient the model such that the longest dimension is left-right, and the shortest dimension is front-back. What are the coordination numbers of Si, Mg, and Ca?
- Focus on the narrow, central part of the model. Tremolite is a "double-chain" silicate. Locate the two linked chains of Si tetrahedra. (Hint: these will occur front to back with the model in this orientation; this is parallel to the c-crystallographic axis.) Describe how the tetrahedra are linked to form each chain. Find the "bridging oxygen" which connects the two chains. If the model were extended in space, predict the location of the next bridging oxygen for additional unit cells in front and behind.
- Continue to focus on the center of the model. Note that the top double chain has the tetrahedra with an apex pointing "down", and the bottom double chain has the free apex pointing "up". What type of crystallographic sites are located in between these double chains? This structure of alternating tetrahedra-octahedra-tetrahedra sites, or T-O-T, forms the basic architecture of the amphibole group. Look at the model from the front side and compare with figure 13.67. The T-O-T structure is also referred to as "I-beams" because of their shape in cross section. Note the relationship of adjacent I-beams how are they connected in the structure?
- Locate the silver balls in the center of the structure. The two silver balls in the front and back of the structure are identified as the M1 sites (M refers to metal, Mg in this case). The three balls in the center are referred to as the M2 sites (on both ends) and M3 (in the center). Note that the gold balls (Ca) have a higher coordination number, and therefore, occupy unique crystallographic sites, known as M4. What is the relative ionic radius of Ca compared to Mg?
- Figure 13.66 is a perspective view of the tremolite structure seen from the "top" of the model (the long dimension is the crystallographic b-axis, and the front-back direction is the crystallographic c-axis). Compare the atomic positions in the model to this perspective drawing.
- Note that some of the expected positions of oxygen (red balls) are occupied by hydroxyl complexes (green balls). Why does this occur?
- Note that there are some very large sites in the structure. These are known as the A-sites. What is the coordination of these sites? These sites are empty for tremolite, but are commonly filled, or partially filled, for other amphiboles. What elements would be expected to occur in these sites? If the A-site is partially filled, what also must happen elsewhere in the structure? (Hint: look up the mechanism for coupled solid solutions.)
- Compare the tremolite (amphibole) structure to the diopside (pyroxene) structure. What aspects of these crystal structures are similar, and how are they different? Look at figure 13.69, 13.70, 13.71 (p. 492-493). A class of related minerals is called "biopyriboles". Note that it is possible to have not only single and double chains, but also triple chains, and these structures can alternate within a single crystal.
- Describe the most likely position of cleavages in this structure (see Fig. 13.67).

Biotite $K(Mg,Fe)_3(AlSi_3)O_{10}(OH)_2$; O=red, Si=black, Mg,Fe=silver, K=gold, OH=green (see Figs. 13.82, 13.83 these are related structures of pyrophyllite and muscovite; p. 500; 13.84, p.502)

- What are the coordination numbers for Si, Mg, K?
- How are the Si tetrahedra connected in this structure (i.e. how many corners are connected to other tetrahedra, in what direction are the unconnected apices of the tetrahedra pointed)?
- Note that the basic structure consists of layers of Si tetrahedra on top and bottom of sheets of octahedral (Mg, Fe) sites; this, again is the T-O-T structure.
- Focus on the atomic sites for K. Are these relatively strong or weak bonds? Where is the most likely place to find cleavage in this mica?
- Look on the "top" of the model (perpendicular to the sheets). What is the apparent symmetry of the "rings" of Si tetrahedra? Note that the sheets of tetrahedra are not stacked directly over the layer below. What is the symmetry of biotite if the stacked layers are "inclined" with respect to each other?
- Compare the biotite structure to the structures of amphiboles and pyroxenes. How are they similar, how are they different?

Alpha Quartz, SiO_2 , Si=black, O=red;

- What is the coordination number of Si?
- What types of bonds are present?
- What is the hardness of quartz? What is the melting point? How are these physical properties related to bond type and strength?
- Compare the structure of diamond and quartz. Are there similarities?
- Describe how the Si tetrahedra are joined in this structure.

Sanidine, $KAlSi_3O_8$; O=red, Si,Al=black, K=gold; fig 13.118, p. 533; Fig. 13.119, p. 534

- Orient the structure so that two gold balls are near the bottom, and the model is standing on two sets of 5 oxygen balls. What are the coordination numbers of Si,Al (black balls) and of K?
- How are the tetrahedral sites connected in this structure?
- Look at the side of the model. Focus on the vertical plane that contains the gold balls in the center. How do the crystallographic sites compare on the left and right side of this model? The long dimension of this model is parallel to the crystallographic b-axis. Compare this view with Fig. 13.118.
- Look down the b-axis. Rotate the model around this axis. Do the atomic positions exactly repeat themselves after 90° , 120° or 180° rotation? (Hint: look down the center of the "channels" as seen in this orientation.)
- All of the tetrahedral sites are essentially the same in this model. What would happen to the symmetry if the structure was "ordered" such that every fourth tetrahedron was somehow unique (e.g. in its size or shape). Try labeling tetrahedral sites in this manner with a small piece of tape and see if the symmetry increases or decreases.
- You now know where the b-axis is in this structure. Use figure 13.119 to help you locate the "crankshaft" structure in this model. (Hint: $a=8.56 \text{ \AA}$, $b=13.03 \text{ \AA}$, $c=7.17 \text{ \AA}$; K&H p. 541; you need to find the unit cell orientation that contains the two largest crystallographic dimensions to get the same perspective as the drawing in this figure.) You will see only a couple of repeat units along the a-axis.

Summary Questions

1. What are the two basic ways that close-packed planes of oxygen can be stacked to form three dimensional crystal structures?
2. In all of the crystal structures you have observed, the various cations have filled voids in layers of anions. Construct a chart that includes the following: number of "nearest neighbor" anions, type of coordination polyhedra, the radius ratio for cations and anions (R_c/R_a) (see Bloss 1971 p. 230-235 or K&H, p. 190-197), and for silicate minerals (with O as the principal anion) the elements that would be expected to go into each site. Look at the periodic table and see if there is a pattern regarding which groups of elements are most likely to occur in different crystallographic sites.
3. For different types of coordination polyhedra in the various models, what is the charge of the cation in the polyhedron, and how much charge is "shared" from each of the nearest neighbor anions? Is the charge on the anion balanced by shared charge from the surrounding cations? Has the overall structure achieved electrostatic neutrality? Is this generally true for the structures that you have studied?
4. Look carefully at the ways in which coordination polyhedra come together to form a 3-D crystal structure (the silicate models are best to review; compare with the perspective drawings in your text book). Do the polyhedra tend to share single points, edges, or faces? Explain this relationship.
5. Focus on polyhedra that have small coordination numbers and contain elements with high valence. Do these polyhedra tend to be concentrated within the crystal structures, or do they tend to be dispersed?
6. You have looked at a number of different types of crystal structures that are representative of a large part of the mineral kingdom. In general, is there a large variety of crystallographic sites in any of the crystal structures, or do the types of crystallographic sites tend to be small?
7. Compare your answers to the above questions with the discussions on "Pauling's Rules" from Bloss (1971, p. 235-245 or K&H p. 197-201). Congratulations! You have just rediscovered the fundamental principles of crystal structures that were first described by Linus Pauling in 1929, and which led to his award of the Nobel Prize for Chemistry in 1954.

Source of Crystal Structure Models

Klinger Educational Products Corp.
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MINERALS AND LIGHT

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INTRODUCTION

When light strikes the surface of a substance, it is split into three parts that are: (1) transmitted through the substance; (2) reflected off the surface; and (3) absorbed by the substance. See Figure 1. How much of the light in each of the categories is determined by the nature of the substance. Substances that allow some light to be transmitted through them are said to be translucent or transparent; those that allow no light to pass through are opaque. When we worked to identify minerals in previous labs, two of the important properties we used were luster and color. Both of these properties have to do with the way a mineral interacts with light; in determining them we consider only the *reflected* light.

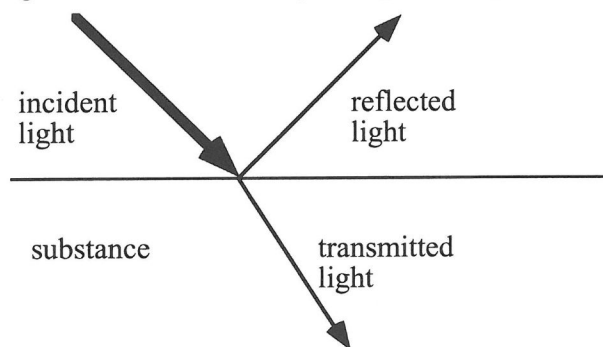


Figure 1. Light is split into three components: transmitted, reflected, and absorbed. (Absorbed light energy is transferred to atoms of the substance and is not shown here.)

Though many minerals are opaque, such as pyrite and graphite, even more are translucent. Today, we will examine translucent minerals (and some other substances) and observe the light *transmitted* by them.

POLARIZED LIGHT

Normal light, whether it comes from the sun or a light bulb, can be considered to vibrate rapidly at right angles to the path it travels. Usually, the vibration takes place in all directions perpendicular to the ray path simultaneously; or the vibration direction is spiralling so fast that it might as well be going in all directions. However, polarized light is light that is constrained to vibrate in only one direction. See Figure 2.

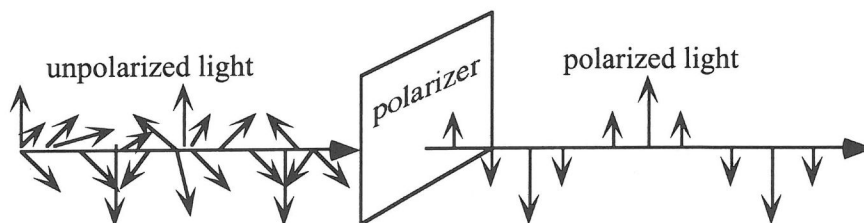


Figure 2. Polarization of light. Light ray is moving from left to right. Arrows indicate vibration direction and magnitude. The polarized light vibrates only in the plane of the page, while the unpolarized light vibrates in all possible directions at 90° to the ray.

One way to help visualize this is to take a strip of an index card and pretend it is a light ray. The long dimension of the card is the direction of a light ray's path; the short dimension shows the vibration of the light ray. When light is polarized it is as if all the possible light rays traveling in a given direction were filtered so that they all vibrate parallel to one another. This can be shown by using a comb to represent a polarizer; the card (vibrating light ray) can only pass through if it is parallel to the teeth of the comb. A polarizing filter does the same thing with unpolarized light: light is polarized in one direction (which we call the "vibration direction") as it passes through the filter, so that all rays are vibrating parallel to one another.

Polarization by reflection

We frequently encounter another type of polarized light, especially on a sunny day when the sun is low in the sky. When light rays reflect off a flat surface, they are partly polarized in a direction parallel to the surface. The shinier and smoother the surface, the stronger the polarization. This is the reason that our eyes are affected by reflected glare off road surfaces, the hood of our car, the surface of a lake, or a snow-covered field.

- What is the direction of polarization for all of these surfaces?

You can observe this type of polarization in the lab by moving to a position from which you see reflected glare (preferably from sunlight) off a clean smooth lab bench.

- Using a small polarizing filter that has been marked with its direction of polarization, determine the direction of polarization of the reflected light.

Because so much of the glare is vibrating the same way, manufacturers of sunglasses have devised a means of eliminating it. They do so by using polarizing filters in the lenses of the sunglasses.

- What is the direction of polarization of polarized sunglass lenses?

Now, imagine yourself, early on a summer evening, driving a car in a large city along a busy street lined by skyscrapers. The fronts of the skyscrapers are covered with huge sheets of plate glass. The street bends so that the low-angled light from the sun suddenly reflects off the buildings and nearly blinds you. You have your polarizing sunglasses in your pocket.

- How do you avoid an accident?

Polarization by minerals

Is reflection off a surface the only way that polarization can occur? No, in fact the polarizing filters, and polarizing sunglass lenses, polarize light by absorbing the light that is not vibrating in the "correct" direction. But we're not here to talk about sunglasses. What do translucent minerals do to the light that is transmitted through them?

In the next part of this exercise, we will use a clear rhombic piece of the mineral calcite. PLEASE TREAT THIS SPECIMEN CAREFULLY! Although most translucent minerals interact with light in the same way as calcite, we use calcite because the effects are much easier to see.

- Place the calcite rhomb on this paper directly over these words. Describe what you see.
- Now, using your small polarizing filter, test the vibration direction of the light associated with the images you see through the calcite. You can describe the polarization direction(s) by relating it(them) to the shape of the calcite, noting that the rhombus has two acute angles and two obtuse angles. Draw a sketch to show the top view of the rhomb and the polarization direction(s).

ISOTROPISM AND ANISOTROPISM

What you have just observed is the phenomenon of "double refraction." Minerals such as calcite actually split transmitted light rays in two! And you have discovered that the two rays actually are polarized in different directions (at 90° to each other) by the calcite. Substances that behave this way are said to be optically anisotropic. Isotropic substances, on the other hand, do not split light in two.

What determines whether a substance will be isotropic or anisotropic? It has to do with the arrangement of atoms; for a mineral, it's the crystal structure. If the atoms are arranged in the same way in all directions in a substance, it is isotropic; but if the arrangement is different in different directions, it is anisotropic. As an example, look at the crystal structure models of fluorite and muscovite.

- Would you expect these minerals to be isotropic or anisotropic?

Isotropic materials do not change the vibration of light that goes through them. An easy way to determine whether a substance is isotropic or anisotropic is to make use of polarized light. Use one polarizing filter on each side of a material to be tested, and set their polarization directions at right angles to each other. (This is called viewing under crossed polars.) If all you see is darkness (extinction), regardless of the orientation of the material being tested, then that material is isotropic. If you see light, it is anisotropic.

- Use a portable light box fixed with a large polarizing filter for the rest of this exercise. One student should hold a second polarizing filter above the first. Check to be sure the two filters are at right angles by getting them at the darkest (extinction) position. Now test each of the materials by holding them between the two polarizers. When testing a material, try rotating it a bit, and if it shows some transmitted light, turn it until it is at its brightest. Remember, if it remains dark, it is isotropic (I). If light comes through, it is anisotropic (A). BE SURE TO KEEP THE POLARIZERS' VIBRATION DIRECTIONS AT EXACTLY 90° TO EACH OTHER.

TABLE 1. OPTICAL CHARACTER OF SOME TRANSLUCENT MATERIALS

substance	I/A	substance	I/A	substance	I/A
air		cellophane tape		muscovite	
water		bubble wrap		halite	
cellophane		glass		gypsum	
plastic wrap		quartz		ice (be quick!)	
baggie		fluorite			

Notice the minerals in Table 1. Fluorite and halite belong to the isometric crystal system. In the isometric crystal system, atoms are arranged in the same way along the x, y, and z (a_1 , a_2 , a_3) directions. As it turns out, of all the non-opaque minerals, those belonging to the isometric system are isotropic, while those belonging to other crystal systems are all anisotropic. If you have done some work on crystallography or symmetry, you should see a relationship between the symmetry of a mineral and its optical behavior as well.

- Can you explain why water and glass behave the way they do?

INTERFERENCE COLORS AND THE COLOR CHART

You probably noticed that some of the anisotropic materials showed different colors when you viewed them through crossed polars. These colors, called interference colors, have nothing to do with the actual colors of the materials. What causes interference colors?

Remember how the calcite split the light into two rays with different vibration directions? Well, something more is going on: the two rays actually travel at different velocities through the calcite! By the time the slower ray reaches the end of the mineral, it lags behind the faster ray by a certain distance. It is this lag distance (also referred to as *retardation*) that determines what interference color you see. The difference in velocity between the two rays is a property of each specific mineral (usually expressed as *birefringence*).

There is one other factor that affects interference colors. Here's an analogy that may help. Assume there are two runners competing in a race; neither runner ever gets tired, so they each run at a constant speed, but one runs faster than the other.

- For these two runners, what will determine the lag distance between them at the end of a race?
- How does this relate to the discussion on interference colors?

Examine the interference color chart. Notice there is a specific sequence of interference colors, going from black to gray and white at the left end of the chart, out to yellow, orange, red, blue, and so forth, and becoming more washed-out and pastel in appearance toward the right. (Actually there is no right end to the chart, but the colors would fade to a whitish hue so that the colors would be indistinguishable.)

- Where have you seen these colors before? (Hint: If you said a rainbow, you're wrong! Think again!)

Each of the colors on the chart corresponds to a specific lag distance between the fast and slow rays; the units are nanometers (nm; $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$ or $1 \times 10^{-6} \text{ mm}$). Look at a few of the anisotropic substances again, and see if you can match their interference colors.

- Tape a piece of cellophane tape to a glass slide and determine its lag distance and interference color, referring to the color chart.
- Now assume that the velocity difference between the two rays for the cellophane tape is 0.004 (no units). Determine the thickness of the cellophane tape using the simple formula:
$$\text{lag distance} = (\text{thickness}) \times (\text{velocity difference})$$

INTERFERENCE COLORS AND STRAIN

When a translucent substance is deformed, bent, or heated, its optical properties commonly change. In fact, isotropic materials can become anisotropic when they are strained. Certain plastics and glasses are tested for strain using cross-polarized light. The higher the interference color, the greater the strain. Engineers use this technique to show where a material might break. As an example, take the plastic baggie and stretch it diagonally. Pull hard until it begins to tear.

- Describe what you see when the baggie is viewed between crossed polars.
- For another example, take the molded piece of clear plastic (a plastic box divider) and examine it between crossed polars. Where is the strain the greatest? Draw a sketch.

COMPENSATION

Let's return to the runner analogy.

- Suppose we doubled the length of the race. What would happen to the lag distance?
- What would happen if you doubled the thickness of the tape? Try it! Describe what you see. You may want to add on more layers of tape, in stair-step fashion, making a sort of "wedge" of tape.
- What do you think would happen if you put a strip of tape on at right angles to the first? If you like the track analogy, this would be like a two-lap relay race where the fast runner hands off to a slow runner, and the slow runner hands off to a fast runner. What would be the lag distance at the end of the race?
- Try it with the tape and describe what happens.

With cellophane tape, and all other anisotropic substances, the fast ray and slow ray have a specific relationship to the atomic structure of the substance. For example, in the tape, the slow ray vibrates parallel to the long dimension of the tape, and the fast ray vibrates across the width of the tape. When you place one strip of tape on top of another in the same orientation, the lag distances (and interference colors) are added; when you place them at right angles, they subtract.

Using a glass slide with one strip of tape, you can determine the fast and slow directions of other substances, merely by seeing if the interference colors add or subtract. If they add, then the fast direction of the tape is parallel to the fast direction of the tested substance; if they subtract, the fast direction of the tape is parallel to the slow direction of the tested substance.

THIN SECTIONS AND THE POLARIZING MICROSCOPE

Some minerals are opaque, some are isotropic, and many are anisotropic. Furthermore, many minerals may have their own "natural" color. But all anisotropic minerals have a specific velocity difference, and therefore show a characteristic range of interference colors. Because these properties are so useful in identifying minerals, geologists use a special microscope with built-in polarizing filters. They also use thin sections of rock. These are prepared by cutting a slice of rock, gluing it to a glass slide, and grinding it down to a thickness of 0.03 mm. By making the thickness the same for all minerals in the rock, the interference colors that you see will be determined only by the velocity difference of each specific mineral.

Examine your thin section. Before inserting the upper polarizer, first find an opaque mineral. Opaque minerals appear black no matter how they are oriented. All the minerals that are not black are translucent. Now find an isotropic mineral. These will not allow light to pass through when viewed between crossed polars, so if you insert the upper polarizer, and a grain turns black, and stays black as it is rotated (along with the microscope stage), then it is isotropic. All the other minerals are anisotropic minerals, and you should be able to determine some of the interference colors. Do you see why this type of microscope is so useful to geologists?

INTERFERENCE FIGURE DEMONSTRATION

If you have time, you may want to check this out: Take a flake of muscovite and set it on the microscope stage. Get it in focus, then cross the polars and switch to the highest power objective lens. Now following the instructor's guidance, obtain an interference figure. Surprised? What could possibly be the origin of this image?! Take a course in optical mineralogy and find out!

NOTES AND SUGGESTIONS FOR THE INSTRUCTOR

Optical Mineralogy and thin sections just blew me away when I first was exposed to them. (Of course that was the psychedelic 60's!) Because of my experience, I've always thought that we might attract a major or two if we introduced first-year students to interference colors and such. Therefore, this exercise is primarily intended to be used in an introductory (physical) geology class, perhaps for advanced students or as an extra credit project. It may also be appropriate as a brief introduction ("teaser"?) to optics in a mineralogy or optical class. If using this for more advanced students, remember to translate lag distance as retardation, and velocity difference as birefringence, if those are terms you want them to understand and remember.

The only significant expenses in setting this lab up are the light boxes and the polarizing film. Both are available from Edmund Scientific. The light boxes are small (12.5 in x 9.5 in) and expensive (\$74), but we invested in 10 of them because I also plan to use this for schoolroom visits and science workshops. I'm sure there are less expensive alternatives. The polarizing film is about \$38 for a huge (14" x 24") sheet. We cut these and inserted them on the light boxes, and had thin glass plates cut to cover and protect them. All can be secured neatly with the screws on the lids of the light boxes. Every team gets a light box and a small container with all the other "stuff" mentioned in the exercise, including an index-card "light ray" and a cheap comb.

It is nice to have an overhead projector handy so you can show the entire class some of these phenomena. (This can be done to as large a lecture class as you might have. It has been suggested that two polarizers with a big sheet of muscovite on an overhead can provide a motivational factor.) You will (or may) also want: polarizing sunglasses; large cleavage sheets of clean clear muscovite; good rhombs of iceland spar; interference color charts; thin sections of a rock with opaque, isotropic, and anisotropic minerals (preferably several anisotropic minerals each with distinct birefringence; a good thin section is a garnet-staurolite-white mica schist with fairly robust magnetite, ilmenite or graphite.) Please pass on your suggestions and comments.

The story about the sunlight polarized off the skyscrapers is true--it happened to me during the same semester that I was taking optical mineralogy. I had to drive to New York City to help move my sister from one apartment to another, and I was already nervous about driving in the city. I must have looked funny driving down the busy street with my head sideways and a big grin on my face. The incident really made me understand polarization better! I always recommend to my students that when they buy sunglasses, buy only polarizing sunglasses. They are so much more fun to play with (e.g. you can always see interference colors looking out an airplane window)!

Regarding the experiment using the clear calcite ("iceland spar"): I have seen so many references to the "strange" or "amazing" double refraction of calcite, that I am sure people treat it as an oddity. I think they should know that all anisotropic materials have double refraction, it's just that calcite has a really serious case of it. If you have ideas of good materials for determining isotropism and anisotropism, please pass them on. You could certainly use hair. In buying tape, buy the cheapest tape possible. Don't buy the "magic invisible" tape, it won't work. For ice, freeze water in a petri dish and quickly place it between crossed polars. Ice cubes don't work well.

In introducing the interference color chart, they will all think they recognize the colors of a rainbow. It is sometimes fun and effective to take them outside on a wet day to see an interference film on the asphalt. Soap bubbles or films and new (stuck together) glass slides are also good.

For the questions about the cellophane tape, I measured approximate refractive indices for my cheapo tape at about 1.532 parallel to the length and 1.528 perpendicular, so the birefringence was 0.004. You may need to modify this to suit your tape. If the retardation for one strip of tape is down in the 1° gray to white region, you may want to double or triple the thickness to get to a more distinctive interference color. This is a sort of procedure that even more advanced students should learn to apply. At the very least, they should get used to using something like this to tell 1° white from high-order white. By the way, with quartz wedges costing between \$500 and \$1,000 these days, I think everyone should be using homemade "tape wedges!" Incidentally, our tape turned out to be about twice as thick as a thin section!

The plastic box dividers were retrieved from damaged boxes used in mineral and rock labs in physical geology. They gave spectacular patterns of interference colors.

EXPERIMENTS IN CRYSTAL OPTICS

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INTRODUCTION

In most crystalline materials, the speed of light varies with direction. This phenomenon, optical anisotropy, is the principal subject of optical crystallography. The most striking feature of optical anisotropy is double-refraction (or retardation). Macroscopically, it manifests in three ways:

- In traveling through the crystal, an incident light ray is broken into two rays,
- rays emerging from the crystal are polarized,
- a crystal, sandwiched between crossed polars, shows interference colors in transmitted light.

The classic physical optics textbook approach to double-refraction starts from Huyghens constructions of wave fronts and from the optical indicatrix. Optical indicatrices are useful for a systematic description of optical properties in crystals, but students do not usually consider them an easy subject, and, therefore, shy away from optical crystallography. This is unfortunate since a basic understanding of optical crystallography is prerequisite to a correct interpretation of phenomena observed with the polarizing microscope, the most commonly used tool for the detailed study of rocks.

Generally, students are comfortable with simple optical terms like reflection and refraction, while it is uncommon that they actually have seen double-refraction and noticed that crystals polarize light. Many have an unnecessarily complicated idea about vibration directions, interference colors, and interference figures; they assume such phenomena always require a microscope to observe. This is not so. Students well trained in thin section microscopy are often surprised that interference figures can be made visible macroscopically.

The purpose of the experiments below is to impart an intuitive understanding of the interaction between light and crystals and, thus, of optical crystallography. This will help to demystify what is seen in the polarizing microscope, and will better prepare the student for the introduction of optical indicatrices as 3-D models to describe the directional dependence of light velocities, and thus refractive indices in anisotropic crystals.

Background

The following demonstrations and exercises are designed for use in an undergraduate course in mineralogy or optical crystallography. If students are not familiar with elementary optics, I suggest a brief explanation, or recapitulation, of (a) Snell's Law (i.e. the Law of Refraction: rays at boundary surfaces, index of refraction, speed of light in matter) and (b) polarization of light (unpolarized light, polarized light, polarizer, analyzer, plane of polarization). Furthermore, students should have a basic knowledge about crystal systems, crystallographic axes, etc.

CLASS ROOM DEMONSTRATION OF DOUBLE REFRACTION

Materials needed:

- Optical bench, 100 cm
- Helium-neon laser^{#)}, 0.2/1.0 mW
- 1/4-lambda filter^{#)}
- 2 polarizing filters with angular scale^{#)}
- Lens, $f=150$ mm^{#)}
- Table^{#)} or ring^{*)} to hold crystal
- Clear calcite cleavage rhombohedron (at least 30mm x 40mm x 60mm).
- Clear quartz prism (diameter at least 30mm)

Optical bench, laser, lens, filters etc. are standard equipment in physics departments and used in lab classes on geometric optics. At our university, we borrow this equipment from the Physics Department.

Experimental set-up and preparations

The experimental setup is illustrated in Figures 1A and 1B. I use a HeNe-laser for a light source (maximum output 1mW, with an integrated grey filter the output can be reduced to 0.2mW). The laser is clamped to the optical bench. The laser beam should be unpolarized. But since unpolarized lasers fluctuate their polarization state, it is best to make the beam circularly polarized by inserting a 1/4 lambda plate in the laser beam. Mount the calcite rhomb with the rhombohedron face normal to the incident ray. If the rhomb is held by a table, plasticine helps fix the crystal in the correct position.

Two parallel rays leave the crystal: the ordinary and extraordinary ray. Depending on the rhombohedron size, the spacing between these two rays is on the order of a few millimeters or, at most, a centimeter. In classes with a larger audience, most students will be too far away to actually see the two emerging rays as distinctly separate. This may be remedied by placing a convex lens in the passage of rays. The lens allows one to project the points of emergence on to a screen. (Points of emergence are the points where the two beams emerge from the crystal.) The blackboard or a wall will do as a screen. With sufficient distance from lens to screen (several meters), the images of the two points, and thus of the two rays, will become visible to students seated far away.

If the incident laser beam, ordinary ray and lens axis all are coaxial (they should be), the ordinary ray traverses the lens undeflected. The extraordinary ray is refracted by the lens and crosses the ordinary ray at the focal point. Beyond the focal point, the two rays diverge and can, therefore, appear as two clearly separate spots on the screen (Fig. 1B). The spacing between these two spots increases with decreasing focal length of the lens, and with increasing distance between lens and screen.

^{#)} Laser, filters, lens and table are mounted on stems. These stems fit in holders clamped to the optical bench.

^{*)} For a slightly more sophisticated version of the experiment, the table is replaced by a ring (Fig. 1) mounted on a stem.

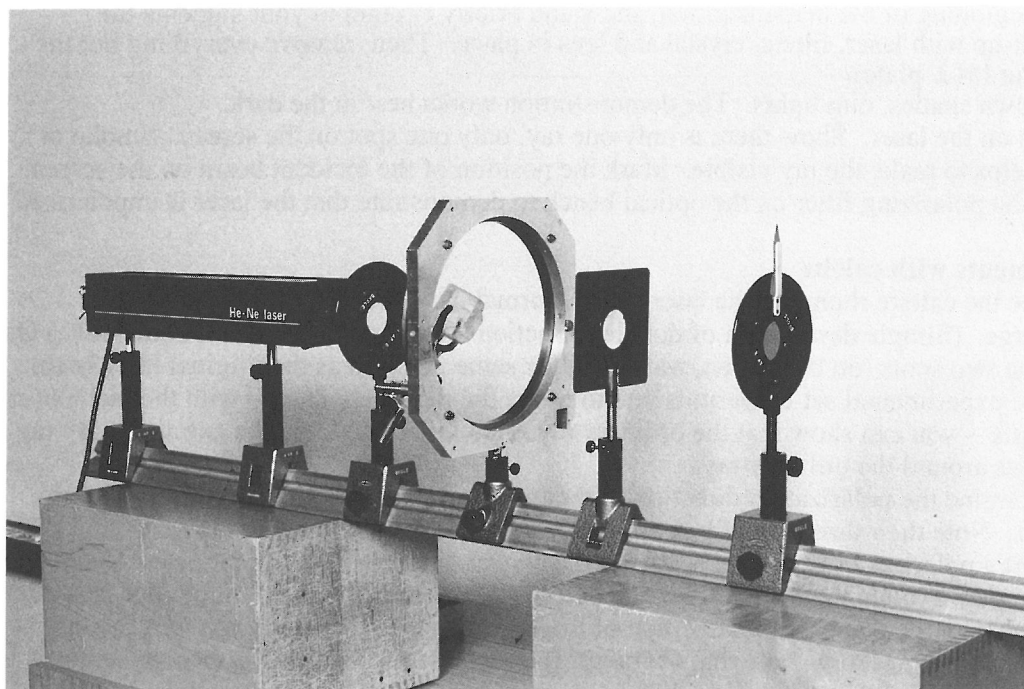


FIGURE 1A. Experimental set-up for the demonstration of double-refraction in calcite. From the left: laser, $\lambda/4$ -plate, calcite rhomb, lens, analyzer.

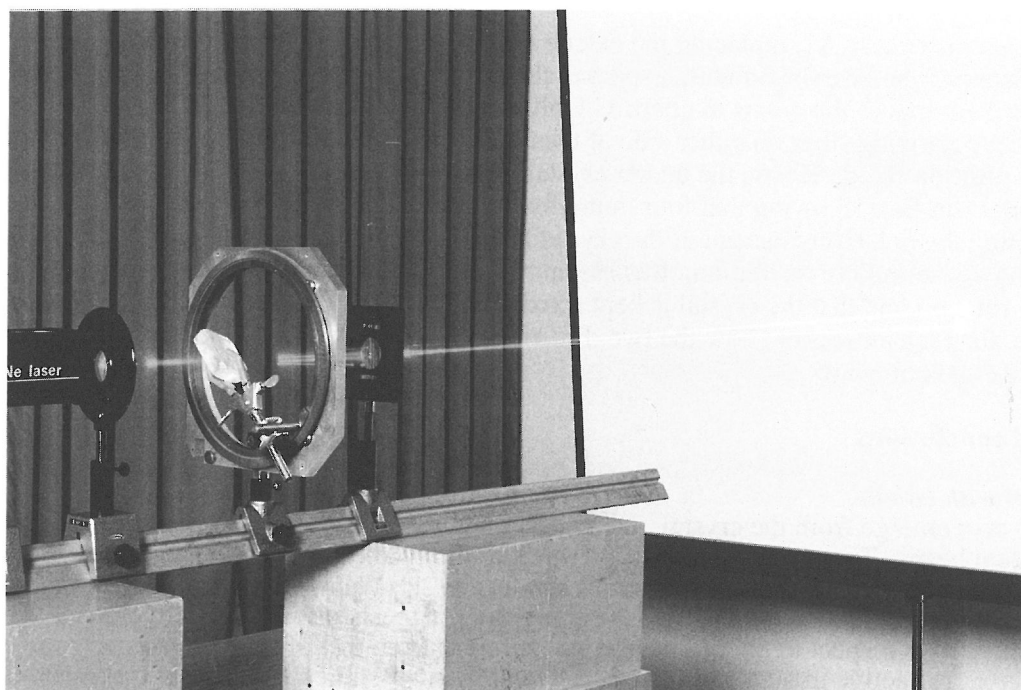


FIGURE 1B. Passage of rays. If the calcite is not perfectly clear and contains cracks, at very close distance, very thin beams may be noticed. From farther away, only the primary beam and the emerging beams are visible.

The emerging rays also pass through a rotatable polarizing filter.

At the beginning of the demonstration, show and briefly explain to your students the complete set-up with laser, filters, crystal and lens in place. Then, remove everything but the laser (and the $\frac{1}{4} \lambda$ plate).

- Pull down shades, dim lights. The demonstration works best in the dark.
- Switch on the laser. Show there is only one ray, only one spot on the screen. Smoke or dust helps to make the ray visible. Mark the position of the incident beam on the screen.
- Place the polarizing filter on the optical bench to demonstrate that the laser is unpolarized.

A. Experiments with calcite

1. Place the calcite rhomb in the laser beam (normal incidence). One ray enters, two emerge. (Simple description of double refraction: "One ray goes in, two come out".) One of the two spots (on the screen, wall) is in the same position as the original laser beam.
- 1a. If the experimental set-up permits you to rotate the rhombohedron -- with the incident ray as axis -- you can show that the ordinary ray is stationary and that the extraordinary ray circles around the ordinary ray.
2. Determine the polarization direction of the two emerging rays by using the polarizing filter. Note their direction of polarization with respect to the c-axis of the crystal.
3. Insert a polarizer between the laser and the crystal, making the incident beam plane-polarized. Rotate the plane of polarization by turning the polarizer. Show that this does not change the planes of polarization of the emerging beams; it only changes the intensity of the two rays. Also, note that every 90° rotation one of the rays will become extinct.
4. Rotate the crystal about the incident beam (which is normal to the rhombohedral face). Show that planes of polarization of the emerging beams rotate with the crystal, (i.e., that they are fixed with respect to its c-axis.)

B. Experiments with quartz

1. Repeat experiment A1, replacing the calcite rhomb by a quartz crystal. Ensure normal incidence of the laser beam with respect to the prism face of the crystal (i.e., the laser beam is normal to the c-axis in quartz). Only one ray is visible.
2. Place a polarizing filter on either side of the quartz crystal. Cross the two filters and keep their position fixed. Rotate the quartz crystal (not the polars!) 360° about an axis normal to the prism face, showing that four mutually perpendicular extinctions occur.
- 2a. Rotating the polarizers instead of the crystal leads to the same result: Four extinctions during one complete revolution. It is essential that both polarizers remain crossed during their rotation and that the crystal is kept fixed.
3. Note, for each extinction, how the two directions of polarization are oriented with respect to the c-axis in quartz.

Results and conclusions

Experiments with calcite.

1. Two rays emerge from the crystal, one undeflected, the other deflected with respect to the incident beam. The undeflected ray is termed 'ordinary', because it follows Snell's Law. The deflected ray does not follow Snell's law and so it is called the 'extraordinary ray'. The different refraction behavior of these two rays suggests that the refractive index effective with respect to the ordinary ray is different from that of the extraordinary ray. Different refractive indices result from different light velocities. Thus light traverses the calcite at two different speeds, at the same time.
2. The emerging rays are examined with a polarizing filter. During one complete turn of this polarizer, each of the rays disappears twice; extinctions are 90° apart. This proves

that the emerging beams are linearly polarized, and their planes of polarization are mutually perpendicular.

3. Extinction always occurs in definite positions of crystal and polarizing filter relative to each other. Consequently, planes of polarization (vibration directions) in the crystal are fixed with respect to crystallographic directions: one is parallel to c , the other normal to c (Fig. 2A).

Experiments with quartz.

1. The incident beam is not broken into diverging beams.
2. Rotating the quartz prism between crossed polars (experiment B.2) yields four extinctions, 90° apart. The experiment proves that light emerging from the crystal has two planes of polarization and that these are mutually perpendicular.
3. The planes of polarization are fixed with respect to crystallographic directions. Their orientation relative to the c -axis is the same as in calcite: One is parallel to c , the other normal to c (Fig. 2B).

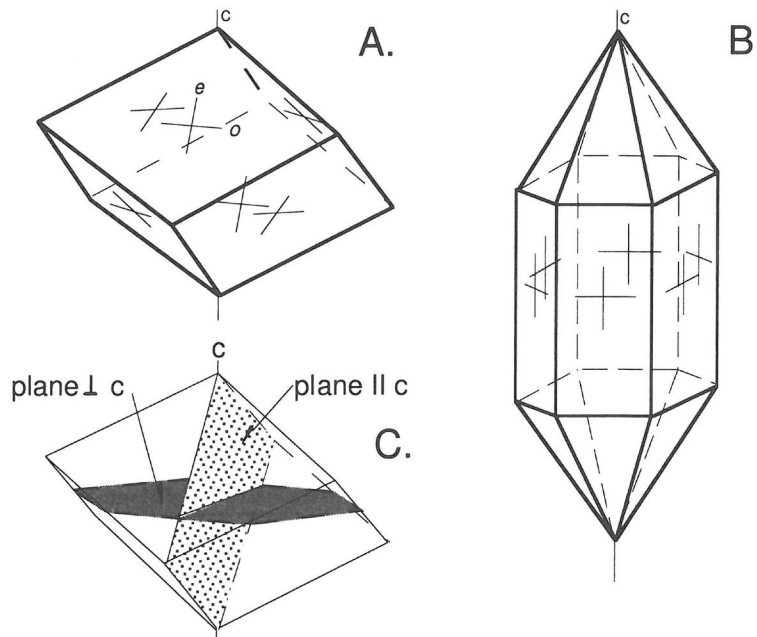


FIGURE 2. Directions of polarization (vibration directions) are marked as crosses on rhombohedral faces of calcite (A) and on prism faces of quartz (B). - Vibration directions of rays: e - extraordinary, o - ordinary. (C) Calcite rhombohedron with planes parallel to c and normal to c .

Explanations

The experimental results may be interpreted by using crystal structure drawings for calcite and quartz. In the calcite structure, carbonate ions form planar CO_3^{2-} triangles oriented normal to c (Fig. 3). Vibration directions (planes of polarization) were found to be parallel to c and normal to c (Figs. 2A, 2C). Consequently, waves traveling through calcite either oscillate parallel to the plane

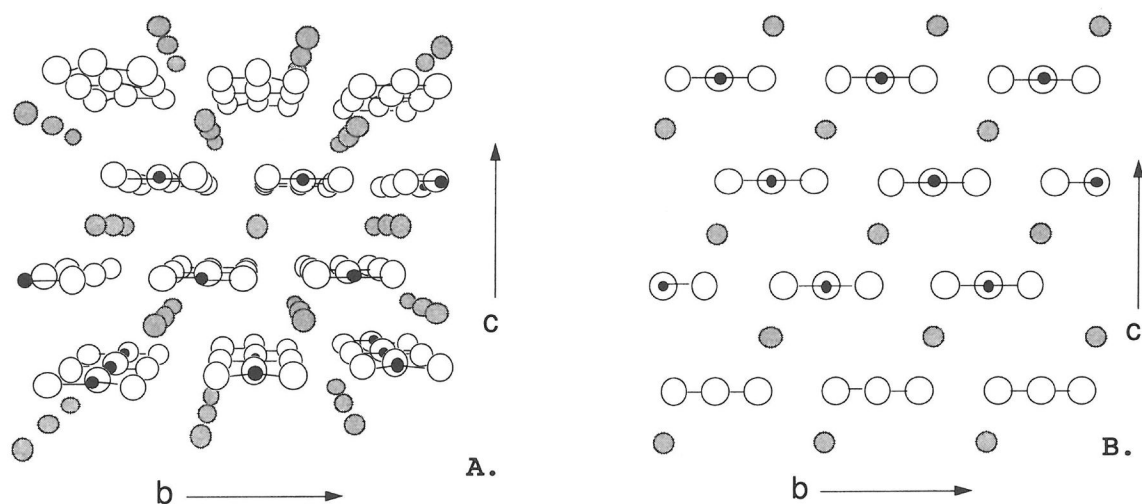


FIGURE 3. Crystal structure of calcite (CaCO_3). Spheres represent atoms: white - oxygen, black (small) - carbon, dark gray (large) - calcium. A. Perspective view along direction perpendicular to c (and b), [210]. B. Projection onto c, b plane, (100). CO_3^{2-} groups are arranged in planes normal to c. In directions perpendicular to c, oxygen atoms are densely packed, distances between them are relatively small. In directions parallel with c, distances between oxygen atoms are relatively large. (Figure generated with ATOMS).

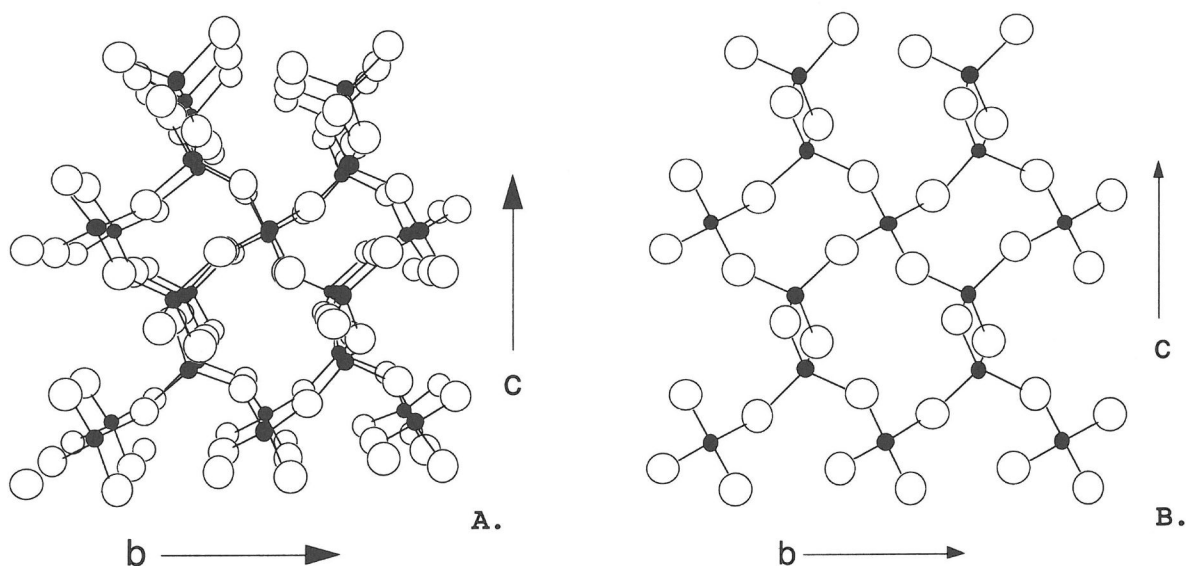


FIGURE 4. Crystal structure of quartz (SiO_2). Spheres represent atoms: white - oxygen, black - silicon. A. Perspective view along direction perpendicular to c (and b), [210]. B. Projection onto c, b plane, (100). - Oxygen atoms are distributed almost evenly in this structure, distances between them are almost the same in all direction. (Figure generated with ATOMS).

Of the atomic species in the structure, oxygen is the one with the highest degree of atomic polarizability and, therefore, the one to most strongly interact with light. The influence of the other atoms is negligible. Light waves vibrating parallel to the CO_3^{2-} planes interact with many more oxygen atoms than waves normal to them. Interaction with (the highly polarizable) oxygen atoms slows light down. The lower the velocity, the higher the refraction. Thus, waves vibrating normal to c travel much slower and have a higher refractive index, than waves vibrating parallel to c. The crystal structure of calcite shows why the maximum double refraction in this mineral is very high ($n_e - n_o = 0.17$). In planes perpendicular to c, oxygens are much more closely packed than in planes parallel to c (Fig. 3).

Compare this to the crystal structure of quartz (Fig. 4): oxygens are almost evenly distributed in all directions. Therefore, it is plausible that light rays with their vibration directions perpendicular to c and parallel to c travel through the crystal at very similar speeds and thus differ very little with respect to their indices of refraction. The maximum difference of the refractive indices in quartz ($n_e - n_o = 0.009$) is small in comparison to that observed in calcite.

PREPARATION OF HANDS-ON EXERCISES

Materials

Each student is given a kit with the following materials:

- 2 pieces of sheet polarizers (50mm x 50mm),
- quartz crystals with hexagonal prism, length > 4 cm, diameter > 2.5 cm,
- calcite rhombohedron, minimum length of smallest edge: 20mm (preferable are rhombs with distinctly different edge lengths, e.g., 20mm x 25mm x 30mm),
- muscovite sheet, minimum size: 30mm x 30mm, thickness to yield 2nd - 4th order interference colors,
- thin sections of rocks (e.g., basalt with phenocrysts, granite, dunite),
- felt tip pen (water soluble),
- interference color chart,
- quartz section cut normal to c (diameter: 25mm, thickness: 1mm)*)
- calcite section cut normal to c (diameter: 25mm, thickness: 1mm)*)

Expenses

Estimated expenses for 10 lab kits with the above items (without thin sections) range between \$75 and \$200. The cost depends largely on size and quality of the calcite and quartz samples. Suitable calcite and quartz samples are commercially available by the kilogram from mineral dealers. The clearer these minerals, the higher their price. Quartz and calcite crystals used in the exercises, need not be perfectly clear, but should be transparent enough to see through. Large polarizing sheets (ca. 300mm x 350mm) are available#) for less than \$25. Cut these in squares of 50mm x 50mm, one sheet yields enough polarizers for 20 kits.

Time

The experiments below are easily completed within one and a half hours.

*) If a microsaw is available, such sections are readily cut from ordinary specimen of calcite rhombs and quartz prisms. These sections need not be exactly normal to c. For the exercises, cuts approx. perpendicular to c will do.

#) e.g. Edmund Scientific, TECHSUP@EDSCI.COM.

HANDS-ON EXERCISES

A. Experiments with calcite

A1. Separation of images.

- a) Place a calcite rhomb on a piece of paper (the paper and rhombohedral face are parallel). View a dot (or another object on the paper) through the calcite rhomb.
- b) Note the horizontal and vertical separation of the two images. Use a ruler to measure the distance between the images.

A2. Effect of crystal thickness on separation of images.

- a) Vary experiment (A1a) by using rhombs of different thickness. The point is to observe how the spacing of the images changes with crystal thickness.
- b) Compare the horizontal separation of the images for different rhombs.

A3. Distinction between ordinary and extraordinary image.

- a) Observe the images of the dot, while rotating the calcite about an axis normal to both the paper plane and the rhombohedral face.
- b) Which of the two images is 'ordinary' (i.e. obeys Snell's law)? Which is 'extraordinary' (i.e. does not obey Snell's Law)? If it is not immediately obvious, how to recognize the 'ordinary' image, imagine the calcite rhomb replaced by a glass plate of similar thickness. You would then only see one dot, i.e., you would see an 'ordinary image' of the dot. Would you expect this (image of the) dot, upon rotation of the glass plate, to stay in place or to move in a circle?

A4. Polarization.

- a) View an object (dot etc.) on a piece of paper through the calcite rhomb. Place a polarizing filter on top of the upper rhombohedral face. Observe the two images. Slowly rotate the polarizer one full circle about an axis normal to the paper (only the polarizer is rotated, not the crystal). What happens to the images?
- b) Start with the extinction of the one image. By how many degrees do you have to turn the polarizer to make the other image disappear? Referring to rays instead of images, the question is: by how many degrees do the polarization directions of the emerging two rays differ?"

A5. Directions of vibration and c-axis. The images are formed by rays traveling through the rhomb. Extinction of images by the polarizer implies blocking of the image-forming rays (and, therewith, light waves) and proves that they are linearly polarized by the crystal. Blocking of rays (images) occurs when the direction of polarization (or direction of vibration) in the crystal is perpendicular to that of the polarizer.

- a) Use the same set-up as in experiment A4. Turn the crystal back and forth to find the stationary (the ordinary) image and then bring it to extinction by the polarizer. On the upper face of the rhomb draw (use felt tip pen) a straight line for the ordinary, vibration direction in the crystal. Label it "o" for ordinary. (Remember: extinction occurs when vibration direction in the crystal and the direction of polarization in the polarizer are perpendicular to each other.)
- b) Turn the polarizer until the other image (formed by the extraordinary ray) disappears. Plot a straight line for the extraordinary direction of vibration. Label it "e" for extraordinary.

- c) Repeat experiment A5a and A5b for all the other faces of the rhomb.
- d) Locate the c-axis in the calcite rhomb (see Fig. 2C). How are the vibration directions and c-axis oriented with respect to each other? Compare with Fig. 2A.

A6. Alternative determination of directions of vibration. Place the calcite rhomb between two polars in crossed position and view it in transmitted light. One way of doing this is to hold the two polarizing filters in the same hand, for instance by placing one filter between index and thumb and the other between middle finger and ring finger. Hold the calcite rhomb in the other hand and stick it between the polars so that these loosely sandwich the crystal and thus are parallel with two opposite rhomb faces. Use a window or a light bulb as light source.

- a) Keep the filters fixed while turning the calcite rhomb about the axis normal to the polarizers and normal to the rhombohedral face parallel with them. Find the position of minimum light transmission. In this position vibration directions in the crystal are parallel and perpendicular to the directions of polarization of the crossed polars. Mark the directions of vibration on the rhomb faces (for instance with a felt tip pen).
- b) Repeat experiment A6a for the other two sets of rhomb faces.
- c) How are vibration directions and c-axis oriented with respect to each other? Compare with Fig. 2A.

B. Experiments with quartz

B1. Separation of images? Place a quartz crystal on a piece of paper (prism face and paper plane parallel). View a dot through the quartz prism.

B2. Polarization. Redo experiment A6 using a quartz prism. Place the polarizing filters in crossed position on either side of opposite prism faces. View the prism against the light. Keep the filters fixed while turning the quartz crystal about the axis normal to the polarizers and normal to the prism face. Find the position of minimum light transmission and mark the directions of vibration on all the prism faces. How are the vibration directions oriented with respect to the long axis of the prism (i.e. with respect to the c-axis)? Compare with Fig. 2B.

C. Experiments with muscovite

C1. Polarization. Place a cleavage piece of muscovite between two polarizing filters in crossed position and view it against the light. Keep the filters fixed and rotate the muscovite piece about the axis normal to the polarizers and normal to the cleavage plane. Find the position of minimum light transmission and mark the directions of vibration on the cleavage face.

How are the vibration directions oriented with respect to the planar cleavage (and normal to the planar cleavage)? Which colors are seen in random positions?

C2. Interference color changes with variation of crystal thickness. Cleave the muscovite into thinner sheets. Observe the change in interference colors with changes in thickness. Try to locate the interference colors on an interference color chart.

C3. Interference colors and orientation. Hold the piece of muscovite in a position where cleavage plane and crossed polarizers are normal to the imagined line between the eye of the observer and the light source. Tilt the sheet against this line and observe the interference color. If the light traverses the muscovite at an angle to cleavage, it passes through more crystal. How do the increased angle and thickness affect the interference colors?

D. Observation of interference figures without microscope

Usually, interference figures of crystals are viewed in the polarizing microscope only. In principle, however, observing interference figures is quite simple and does not require a microscope. All one needs is a transparent mineral in form of a thin, sufficiently large⁺⁾ plate or section, and two polarizers. A daylight light source (a window) is best, but a light bulb will do as well.

Interference figures are not images of the object, but represent interference patterns formed by light rays after passage through an anisotropic medium. These patterns become visible when a thin transparent crystal plate is placed between crossed polars and viewed against the light in such a way that the rays passing through the crystal form a large cone with a wide angular aperture (Fig. 5). This implies that the crystal is examined in many different directions at the same time. In other words, the bundle of light rays passing through the crystal is strongly divergent. This form of observation is called *conoscopic*.

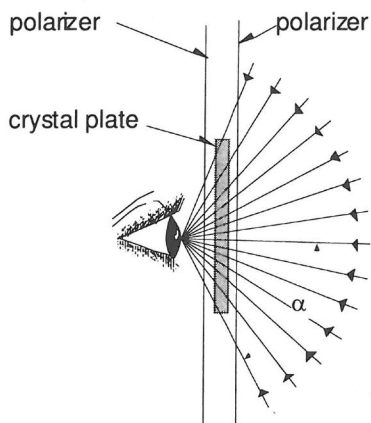


FIGURE 5. Macroscopic observation of interference figures. a - distance between eye and object, α - angular aperture.

At a larger distance to the eye (e.g., 20cm), the crystal plate appears with an overall homogenous interference color. This form of observation is called *orthoscopic* and implies that rays passing through the object are parallel, or almost parallel like in A, Fig. 6: either of the outer boundary rays, which pass at the very edge of the crystal, form a small angle with the central ray. This angle will become smaller yet if the distance between the eye is increased beyond position A, i.e. the rays will become 'more parallel'. Compare this with the opposite situation, the conoscopic passage of rays, where the same crystal plate is placed very close to the eye (Figure 6) and where the angle is thus very large between outer boundary rays and central ray.

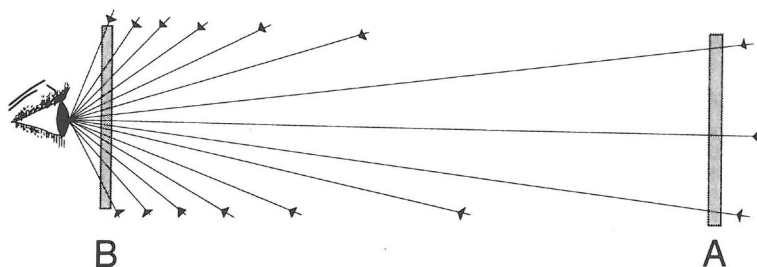


FIGURE 6. Crystal plate at different distances from the eye. A. Large distance. The angle between boundary rays is very small (small angular aperture), i.e. rays are almost parallel: orthoscopic passage of rays. B. Short distance. The angle between boundary rays is very large (large angular aperture): conoscopic passage of rays.

⁺⁾ diameter > 2cm

By diminishing the distance between object and eye, it is possible to zoom from orthoscopic to conoscopic observation. Fig. 6 illustrates this transition: First, in position A, the bundle of rays through the crystal plate is almost parallel, and the angular aperture is very small (orthoscopic observation). With decreasing distance to the eye, rays through the crystal become more divergent, the angular aperture increases. Finally, in position B, the bundle of rays is strongly divergent, and the angular aperture very large (conoscopic observation).

D.1 Experiment with a muscovite cleavage sheet. Place a thin cleavage piece of muscovite between crossed polars. Hold it against the light. Bring it as closely to your eye as possible (Fig. 5, Fig. 6B). Note the dark bands (isogyres) and the curved color bands (isochromes).

D.2 Experiment with sections of quartz and calcite. Place an axial quartz section[§] between crossed polars and observe the interference figure. Note the dark cross (isogyres) and the circular color bands (isochromes). The interference figure observed is a uniaxial figure from a section cut normal to c.

Note that interference figures show interference colors of increasing order from the center outward. These interference colors follow the same sequence as in the interference color chart.

Redo the experiment with the calcite section.

E. Macroscopic observation of thin sections between crossed polars

Observe interference colors of mineral grains in thin sections of dunite, granite, and basalt. Try to locate these colors on the interference color chart.

Explanations

A structural interpretation of double refraction is given above (see explanations to lecture demonstrations). Here, a few additional comments on results, which at first, may appear puzzling.

Experiments A, B and C with calcite, quartz and muscovite show that all three minerals polarize light in two directions. In terms of light waves, this implies that an incident wave splits into two waves, which vibrate in mutually perpendicular planes and travel through the crystal at different speeds. This difference in speed and, thus, in refractive index is easier to explain in calcite than in the other two minerals.

Why is a separation of images/rays observed in the experiments with calcite (A1-A6), but not in the experiments with quartz (B1, B2) and muscovite (C1, C2)? In principle, separation of rays occurs in all of these minerals unless the incident ray is parallel to one of the "principal" vibration directions. In the above experiments with calcite, the incident ray is normal to the rhombohedral face, i.e., it is not parallel to one of the principal vibration directions. Therefore, one can observe a separation of the emerging rays and, correspondingly, a separation of images. In the experiments with quartz and muscovite the incident ray is parallel to one of the principal vibration directions, therefore there is only one ray emerges and no separation is observed.

Why does muscovite show distinct interference colors between crossed polars while calcite and quartz appear white? All three minerals do show interference colors between crossed polars. Yet, not all interference colors are colors in the ordinary sense of the word. - With increasing thickness, crystals produce interference colors of increasing order. Only interference colors of lower order (I-III) show distinct colors (see interference color chart). With increasing order,

[§] An axial section is a section cut normal to c. Recommended thickness: ca. 1 mm

interference colors become paler and, finally, merge into an "high order white", which is indistinguishable from ordinary white light.

Most minerals show distinct interference colors in thin crystal plates (10 μm to 100 μm thick). Muscovite cleaves readily into sheets of such thickness, and, therefore, shows distinct interference colors (see experiment C1-C3). This is not so with the calcite and quartz crystals used in the experiment. Their edge length and diameter measure several centimeters. These specimens are comparatively thick and, thus, yield interference colors of extremely high order (undifferentiated white). This is the reason why they appear colorless.

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LABORATORY EXERCISES AND DEMONSTRATIONS WITH THE SPINDLE STAGE

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Introduction and background

The goal of this lab session is to introduce you to the spindle stage and its possible uses in an undergraduate mineralogy lab. A spindle stage is a one-axis rotation device that mounts on a polarizing microscope and is used to aid in the measurement of optical properties of single crystals. At the undergraduate level, it can be used to identify minerals and to demonstrate the relationships among grain shape, retardation, and interference figures. A natural extension of these uses is undergraduate research on the optical properties of minerals. These notes and other references for the spindle stage are posted at the web site: www.uidaho.edu/~mgunter/opt_min/ss/ss.html.

This lab session would not be possible without the work of Professor F. Donald Bloss, and those fortunate ones who have worked with him over the past two decades to develop, refine, and integrate the methods presented here. Bloss and Light (1973) developed a student spindle stage, Bloss and Reiss (1973) developed a computer program to calculate a biaxial mineral's 2V and indicatrix orientation based upon extinction data, and Louisnathan et al. (1978) refined the double variation method for precise (± 0.0001) refractive index determination of minerals. These works culminated in Bloss' MSA Presidential Address (Bloss, 1978) and a book devoted entirely to the spindle stage (Bloss, 1981). Several computer programs were also developed to aid in reducing data collected with the spindle stage, especially EXCALIBR (Bloss and Reiss, 1973; Bloss, 1979; Bloss, 1981). With the evolution of mainframes to microcomputers, EXCALIBR has been modified to work on both PC's and Mac's (Gunter et al., 1988). Other programs have been developed to aid in refractive index calculation based upon the double variation method (Su et al., 1987) and for routine optical mineralogy calculations (e.g., the relationship between 2V and the principal refractive indices for biaxial minerals) (Gunter and Schares, 1991). Most recently, Barthelmehs et al. (1992) rewrote EXCALIBR, making it much easier to use. All of these programs are available from the web site: www.uidaho.edu/~mgunter/programs/programs.html.

The spindle stage has helped research in optical mineralogy from A (i.e., andalusites, see Gunter and Bloss, 1982) to Z (i.e., zeolites, see Gunter and Ribbe, 1992), with many other optical secrets of minerals unraveled in the middle (e.g., corderites (Armbruster and Bloss, 1982) and feldspars (Su et al., 1986)). These research projects did not use the student spindle stages but the more advanced, and expensive, Supper spindle stage that uses an x-ray goniometer head to mount and hold the crystal. However, student model spindle stages can provide almost the accuracy and precision of the Supper spindle stage. Much more research could be done, especially at the undergraduate level, using the spindle stage. Every department has the necessary equipment (polarizing microscopes) for undergraduates to conduct this type of research. It is hoped this lab session will encourage faculty to use the spindle stage in teaching optical mineralogy, or at least to use it to demonstrate the relationships among grain shape, retardation, and interference figures.

Lab session

Listed below are the necessary steps to implement the spindle stage in an undergraduate lab. Details are provided on how to build a poster board spindle stage (PBSS). Thomas Armbruster, University of Bern, Switzerland, is credited with the idea and original design of the PBSS, which has been slightly modified here. Student spindle stages are commercially available - for example, the detent spindle stage of Bloss and Light (1973) (from McCrone Accessories and Components, 800-622-8122, price = \$50) for those who do not wish to build them. The detent spindle stage is well made and worth the investment if funds allow. If you purchase it, skip step 1 below.

Regardless of the type of spindle stage used, an oil cell must be built in which to view the crystal and to determine its refractive index by the immersion method. To build an oil cell, mount a bent paper clip (or some other type of wire of the correct thickness) to a petrographic slide. Place a drop or two of immersion liquid in the u-shaped paper clip, and place a glass cover slip on top.

Glue a single crystal of a mineral onto the end of a needle, and insert the other end of the needle into the spindle stage. Next, attach the spindle stage and the needle combination to the stage of a polarizing light microscope. Carefully slide the oil cell into the docking port of the spindle stage until the crystal is immersed into the liquid. At this point, you are ready to make optical measurements.

For a complete description of all aspects of the spindle stage refer, to Bloss (1981). Also, Nesse (1991) and Stoiber and Morse (1994) provide brief descriptions of applied spindle stage use. For those rusty in optical mineralogy, refer to Gunter (1992) for a short review, or Bloss (1961), Nesse (1991), or Stoiber and Morse (1994) for thorough treatments.

Please note: As stated above, my intent is to introduce you to the spindle stage, give some idea of what it can do, some "hands-on" experience, and, mainly, provide the resources for you to continue to use the spindle stage in the future. Remember, there is an entire book devoted to the subject (Bloss, 1981), and Bloss taught a semester-long course on its use. And you **will** knock a crystal off the end of needle occasionally, but that's part of the fun!

Lab procedure

The following is a seven-part, step-by-step procedure. The first line in each step (marked with a "*" and in bold) is the action to be taken. The following text in that step are pitfalls, words of wisdom, and hints.

1. Build a poster board spindle stage (PBSS)

materials: poster board, 20-gauge hypodermic needle (Fisher Scientific), petrographic slide, white glue, straight edge, compass, small protractor

Follow the instructions in Appendix A.

2. Build oil cells

materials: petrographic slide, cover slip, large paper clip, epoxy

Follow the instructions in Appendix B.

3. Mount crystals

materials: sewing needle (size #12), fingernail polish, acetone, transparent crystals (0.05 to 0.5 mm), binocular microscope, glass slide, patience

Mounting crystals is a skill that comes with time. At first, it seems very hard, but it gets much easier after you have mounted a few thousand !

Follow the instructions in Appendix C.

4. Align the PBSS and oil cell

materials: PBSS, oil cell, sewing needle

- * **Place a sewing needle (point first) into the PBSS tubing.**
- * **Move the oil cell (using the oil port farther back on the slide) into the docking section of the PBSS and make sure the needle does not hit the slide or the cover slip.** If it does hit, it will need to be adjusted up or down by removing the tubing and changing the height of the hole (in the tubing holder, Figure 1.4). I usually number the oil cells and PBSS's to know which "fit" well together.
- * **Also, check that the needle does not go too far and hit the back of the oil mount (i.e., the epoxied paper clip), or off goes the crystal!**
- * **If the alignment is a problem, then use the oil port mounted at the slide's edge.** This paper clip is a bit thicker than the other, and it will be harder to view an interference figure with this oil port.

5. Attach PBSS to microscope and view a sample

materials: PBSS, polarizing microscope, sewing needle, Scotch tape (about 20 mm wide), patience

- * **Insert the needle without a sample into the PBSS until its end lines up with the pencil marks on the arms of the PBSS.** The needle should be sticking out about 13 mm (see Figure 1.4). The needle will appear a bit loose in the hypodermic needle. This is intentional. The loose fit will help keep you from knocking off the crystal. Later, a tighter fit will be important. This can be accomplished by slightly bending the sewing needle before inserting it, putting a bit of fingernail polish where the needle slides into the tubing, or carefully crimping the end of the tubing. The tubing ends can be exchanged (i.e., the handle taken out and reversed), so one end can be tight and the other loose fitting.
- * **Obtain one piece of tape about 100 mm long and two pieces about 30 mm long.**
- * **Place the long piece of tape across the PBSS between the tubing holder and the protractor.** This separation was designed for the tape to fit into.
- * **Place the PBSS on the microscope stage.**
- * **Using low power, unpolarized light, center the end of the needle in the middle of the cross-hairs.**
- * **Press the tape onto the microscope stage.** Also, add the two shorter pieces of tape to the PBSS arms, being careful to keep them out of the way of the oil cell.
- * **Insert the oil cell and make sure the needle does not hit the slide or the cover slip.**

*** Rotate the microscope stage and the needle around for awhile to make sure everything is near-centered.**

*** Remove the PBSS from the stage by first removing the oil cell and carefully lifting up the tape.** It is not necessary to remove the PBSS to change samples. You can use a small pair of needle nose pliers or tweezers to remove the needle and insert a new one - this is when you get good at it. For now, it is easier just to remove the entire PBSS to change samples.

Later, we will repeat the process with a sample. This was intended to give you some experience without worrying about knocking the crystal off the needle.

6. Sample exercises

- A. determine the refractive index of a mineral - keep the same crystal and change the liquids
- B. find the indicatrix orientation and 2V of a biaxial mineral from extinction data

Please note: I think this is the section I would concentrate on in a mineralogy lab. After you do the next section and demonstrate it to the students, the students should be motivated to build and use the spindle stage to confirm a mineral's identity by observing its optical properties. Also, you will develop the skills needed to assist your students by performing the next section.

7. View grain shape, retardation, and interference figures

materials: samples A & B provided. Sample A is a uniaxial mineral with its c-axis perpendicular to the spindle stage axis. Sample B is a biaxial mineral with its optic normal mounted parallel to the spindle axis.

- * Obtain the sample marked "A" from your glass vial.** You will use the PBSS to observe this grain.
- * Fill the oil cell with 1.510 or 1.512 or 1.514 liquid.** Use the oil port farther back if possible.
- * Repeat the process from "Section 5" above to get the grain, PBSS, and oil cell aligned and affixed on the microscope.**
- * Using low power and plane-polarized light, rotate the spindle axis and observe the shape of the crystal.**
- * What is the crystal's shape?**
- * Switch to cross-polarized light and rotate the spindle axis to obtain a minimum retardation.**
- * Check for minimum retardation while rotating the microscope stage.**
- * Repeat the adjustments on the spindle stage and microscope stage until you find minimum retardation** (i.e., the grain shows 1st order gray or lower retardation as the scope stage is rotated).
- * Check the refractive index of the grain against that of the oil. Is it higher or lower?**
- * What index are you measuring if the crystal is uniaxial? Biaxial?**
- * Rotate the spindle axis 90 degrees and watch what happens to the retardation.**

* **Obtain an interference figure for the sample.** This may be tricky. Sometimes the highest power lens (i.e., the lens with the largest NA) may not be able to get close enough to mineral without hitting the cover slip. These high NA lenses are usually spring loaded, so nothing bad will happen. Two hints are: 1) use the next highest power lens. It will image less of a cone of rays and thus show a smaller portion of the interference figure, but in many cases, especially if the figure is near-centered, one can determine the type of interference figure, and 2) lower the stage so the end of the high power lens is 10-20 mm from the oil cell. Switch to a conoscopic illumination with the high power lens; raise the stage slowly and watch the interference figure form and fill the field. Because of a possible collision between the lens and oil cell's cover slip, I prefer to glue the cover slip down. It will not come off the oil cell and make a mess on the microscope.

* **What is the optic sign?**

* **Rotate the spindle axis 90 degrees and watch what happens to the interference figure.**

* **Replace sample "A" with sample "B".**

* **Obtain an interference figure.** Use the same cautions as above.

* **What is the approximate 2V and the optic sign?**

Please note: I would not recommend having students do this exercise. Instead, I recommend this as a demonstration for you to do. The main problem with having students do this is obtaining and mounting crystals in a preferred orientation, and the inevitable crisis of knocking the crystal off. It takes 5 to 6 minutes to mount and check each sample, so I think this works best as a demonstration. My students seem to enjoy this, and it convinces them that the same mineral will look much different depending upon its orientation. These oriented crystals can also replace the very expensive oriented thin sections, which are also hard to obtain.

For uniaxial minerals, one needs crystals with perfect (001) or (hk0) cleavage. I have used eudialyte and scapolite - this is a good choice for sample "A". (If anyone knows of any other minerals please tell me, especially if they are common.) Given these morphological conditions, the spindle axis can be made perpendicular to c, the optic axis. Another method is to use crystals with no cleavage (e.g., quartz) and view crushed quartz crystals with a binocular microscope set up with cross-polarized light. The big quartz crystals that exhibit low retardation more nearly lie on a circular section. They can then be mounted with their optic axis perpendicular to the needle, and, in turn, the spindle axis.

For biaxial minerals, one needs a cleavage direction that is perpendicular to the optic normal. Gypsum is almost perfect. It has perfect (010) cleavage with $b=Y$ (i.e., the optic normal is perpendicular to the nice flat (010) plane). The problem with gypsum is that you need to mount several crystals (at least I have had to) to find one with minimal "deformation" to show good interference figures. The feldspars, especially K feldspars, are also good candidates. They all have perfect (010) cleavage. For high sanidine, $b=Y$, so it should be perfect, but I have never tried it. Low sanidine has Y perpendicular to another prominent cleavage, (001). These low sanidines can be mounted, with the aid of cross-polarized light, with the needle perpendicular (001) while they are lying on (010) - this is a good choice for sample "B". Both orthoclase and microcline share this same optical orientation and should work as well as low sanidine, but I have not tried them yet. If anyone knows of biaxial minerals that fit this condition, please let me know.

In case we cannot get the interference figures to work, you can view them on my web site: www.uidaho.edu/~mgunter/opt_min/ss/ss.html. I placed short quicktime movies on the web site

demonstrating this exercise. There is a uniaxial mineral, eudialyte, mounted with its c axis perpendicular to the needle; thus, one can rotate from a centered optic axis figure to a centered flash figure. There is also a biaxial mineral, gypsum, mounted with its optic normal parallel to the needle so one can rotate from a centered acute bisectrix, to a centered optic axis, to a centered obtuse bisectrix. There are three movies for each mineral. One movie is made in unpolarized light to show the grain shape as it is rotated. This is good for viewing cleavage, grain thickness, pleochroism, etc. The second movie is made in orthoscopic illumination with polarized light. In this setup, changes in retardation can be observed; anytime a circular section is parallel to the microscope stage (synonymous with an optic axis perpendicular to the stage), retardation is near zero. Retardation is increased to a maximum when, for the uniaxial mineral, the single optic axis is in the microscope stage. For the biaxial case, maximum retardation occurs when the obtuse bisectrix is perpendicular to the stage. The third movie shows how the interference figures change as each sample is rotated about the spindle. It can be instructive to place all three movies for one crystal on the screen at the same time and "rotate" each image the same amount to show how they correlate.

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Appendix A: Building a poster board spindle stage

materials: poster board, 20-gauge hypodermic needle (Fisher Scientific, these come in 6 and 12 inch lengths, #14-82516E and 14-825-15AB), petrographic slide, white glue, straight edge, compass, small protractor

* **Cut two 50 x 50 mm squares and one 10 x 50 mm rectangle from poster board as shown below.** Part A will be the PBSS base, part B will be the protractor scale, and part C will help hold the tubing in place.

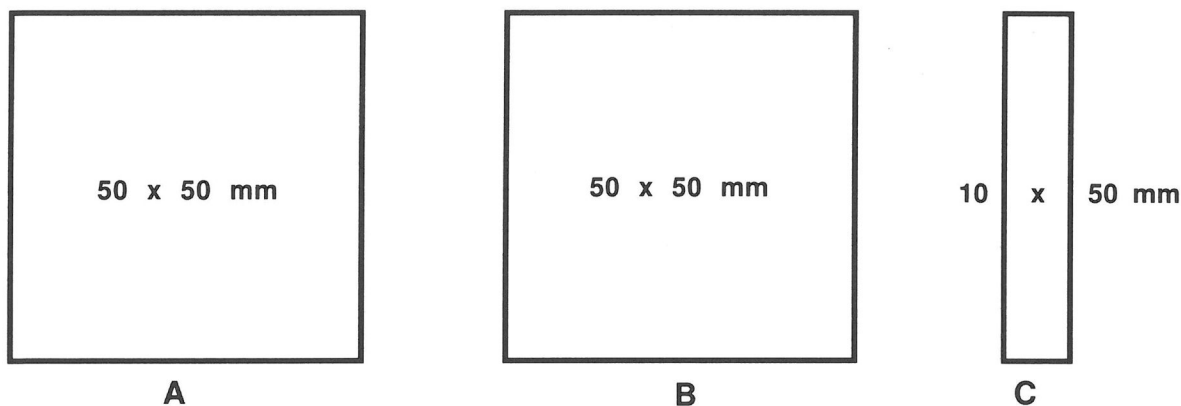


Figure 1.1: Starting material sizes for base (A), protractor (B), and tubing holder (C).

* **Mark all three pieces as below (Figure 1.2), and cut pieces B and C as shown to produce the round protractor as shown in the Figure 1.3.** Part B should first be cut into a circle and then cut in half along the horizontal line.

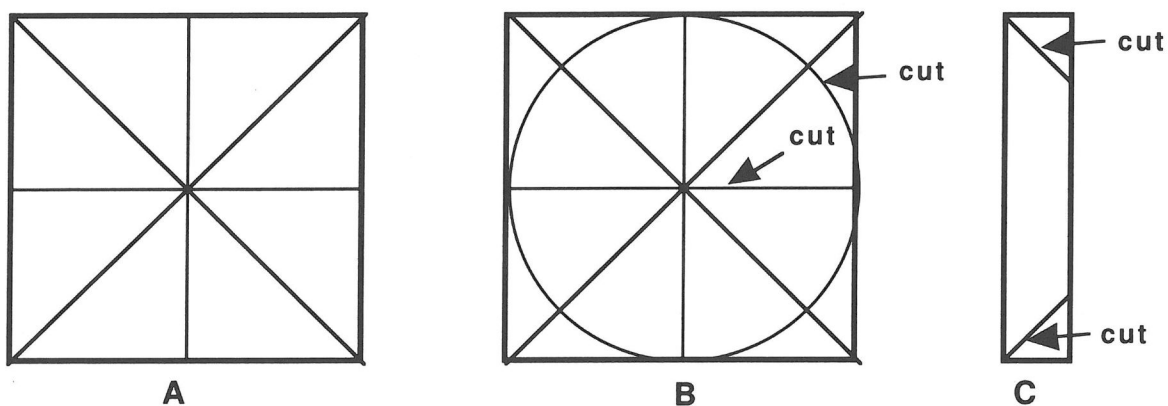


Figure 1.2: Marked-up base (A), protractor (B), and tubing holder (C). B should first be cut into a circle and then cut horizontally. C should just have the edges trimmed.

* **Overlay a petrographic slide onto the base as shown in A below (Figure 1.3).** Use the slide to mark the base and then cut out the marked area. This is the dock for the oil cell to fit into.

* After making the cuts on B above (Figure 1.2), write numbers on it like B below. This is the template (i.e., protractor) to measure the S angles on the spindle stage.

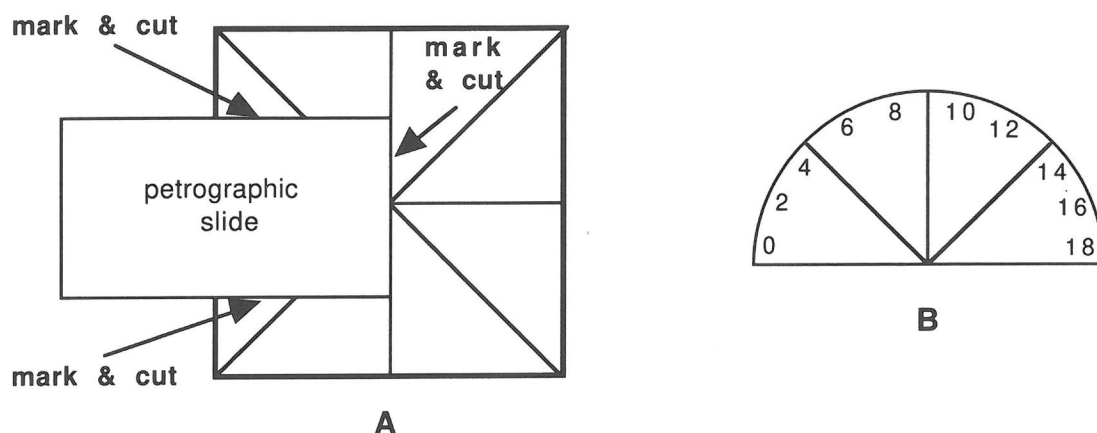


Figure 1.3 : The base (A) with slide overlain for marking the oil cell dock. The protractor (B) cut in a half-circle and numbered.

* Glue the protractor and tubing holder onto the base as shown below (Figure 1.4).

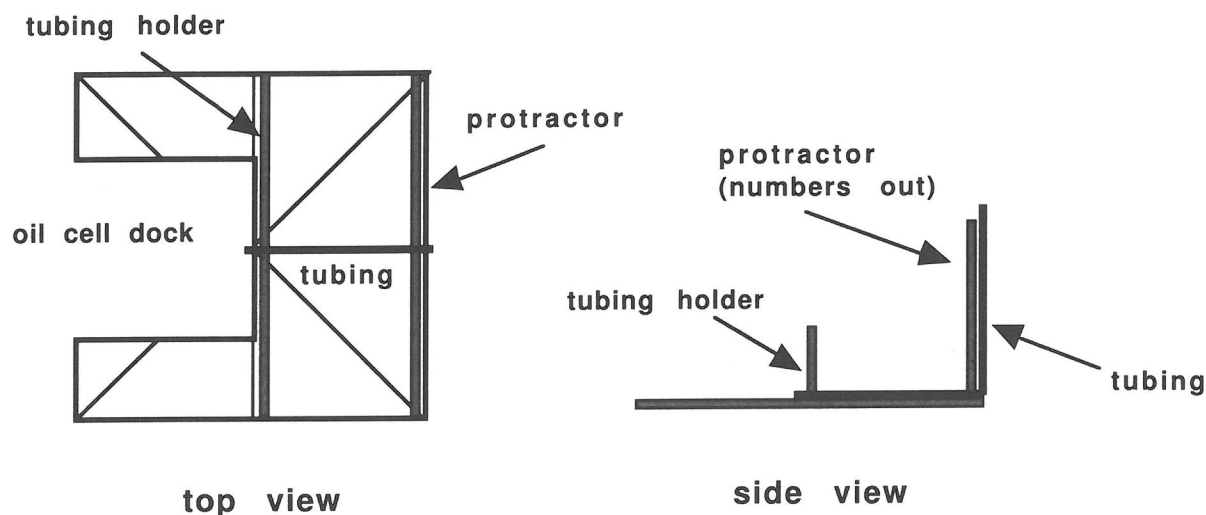


Figure 1.4: Finished PBSS. Left is the top view showing all the assembled parts; right is a side view.

* **Add the hollow tubing.** Cut a piece of 20-gauge hypodermic needle 55 mm long and make a 90 degree bend in the middle. (Hypodermic needles can be cut with a triangular file which does not collapse the needle.) The hole for the tubing in the protractor's and tubing holder's centers can be made with a needle of similar diameter. The two holes should cause the tubing to be parallel to the base so a needle will project from it and be parallel to the oil cell slide. Adjustments may need to be made as described in section 4.

Appendix B: Building oil cells

materials: petrographic slide, cover slip, large paper clip, epoxy

- * **Bend one side of a large paper clip into a small "U" about 5 mm long and epoxy it to the center of a petrographic slide about 13 mm from the end in the slide's center (Figure 2.1 below).** The "U" can be flattened a bit by placing it on a hard surface and hitting it with a hammer. The thicker the "U," the easier the alignment of the oil cell - needle - spindle stage combination. However, the thinner the "U," the better chance one has to see interference figures. These "U"s are the oil ports on the oil cell. We have also used staples and wire to make oil ports.

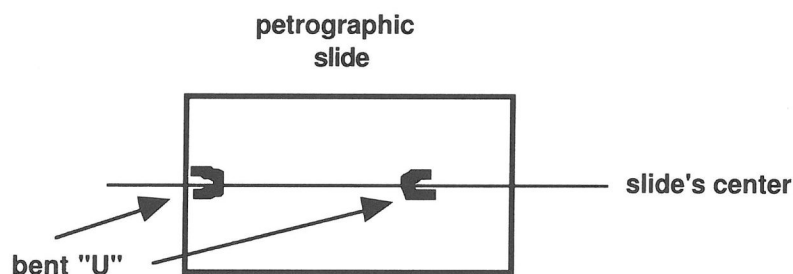


Figure 2.1: A petrographic slide with two bent "U"s epoxied on the slide's center.

- * **Make a second 5 mm "U" and epoxy it on the end of the cell (Figure 2.1).** Less care needs to be taken for alignment with this thicker "U" at the slide's edge.
- * **Cover slips will be placed on top of the "U" to hold in the immersion liquid.** They can be epoxied onto the "U," but surface tension will hold them on. If they are epoxied, they stay on better, but it is harder to clean out the immersion liquid when you need to change it. When the "U" is very thin and the cover slip is epoxied on, air bubbles can form in the oil port. Bubbles can be cleared by holding the oil cell vertically and allowing the bubble to rise. If this does not work, stick a small needle into the bubble while holding the cell vertically. Oil can be removed from the oil port by sticking a small piece of rolled tissue paper between the cover slip and slide.

Appendix C: Mount crystals

materials: sewing needle (size #12), fingernail polish, acetone, transparent crystals (0.05 to 0.5 mm), binocular microscope, glass slide, patience

- * **Obtain several crushed mineral grains of interest (0.05 to 0.5 mm).** They can be sieved if you want to remove the fine and the coarse fractions.
- * **Place them on a glass slide under a low power binocular microscope.**
- * **Locate a good single crystal with the microscope.** Good means not twinned, homogenous, etc. You may not be able to tell if you like the crystal until you see it with the polarizing light microscope.
- * **Get a needle and dip its tip into a drop of fingernail polish.** Super glue, Duco cement, or many other glues can be used; fingernail polish has the advantage of being slow to set, allowing for repositioning of the crystal, and the crystal can be removed with acetone.
- * **Bring the needle next to the crystal and gently touch the crystal with the needle end.** The crystal should stick. If not, add more fingernail polish and try again.
- * **Observe the crystal on the end of the needle.** It should be near-centered at the needle's end. You might want to move it around a little to get it more centered or in a particular orientation. The crystal can be moved by gently pushing it with another small needle.
- * **Reinforce the fingernail polish around the crystal/needle contact.** This can be done by dipping another needle in fingernail polish and working it carefully around the contact; avoid covering the entire crystal with fingernail polish (mineralogists do not care to measure the refractive index of fingernail polish).

INTRODUCTION TO THE SEM/EDS OR “EVERY COMPOSITION TELLS A STORY”

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Purpose

This lab is designed as an introduction to the investigation of minerals with the Scanning Electron Microscope (SEM) and the X-ray analyzer (Energy Dispersive Spectrometer - EDS). We will explore the relationships among the optical image, the backscattered electron image, and the chemical composition of minerals in thin-sections that we have studied optically. Specifically we will examine the interaction of a mineral with a high energy (20 kv) electron beam focused to a diameter of a few microns. Three different detectors of the SEM/EDS will be used to study minerals in thin sections. *Additional concepts that may be introduced in this lab include: formula calculations, solid solution, exsolution, and chemical zoning.*

A. Optical Review of Assigned Sample

Be careful not to touch the polished surface of the thin sections used in this lab as they have been coated with carbon in order to enhance the flow of electrons from the sample when it is in the SEM.

1. Identify the minerals and describe their shape, size, and habits. Note distinctive features within individual mineral grains such as systematic variations in color, pleochroism, extinction, or refractive index (relief).
2. Use the video camera-computer-petrographic microscope to capture and then print an image of an interesting or representative area of the slide. The image should be at a magnification consistent with the grain size. For example, a low power (10X) field of view for a medium grained rock is a good starting point. Try 3.5X for coarse-grained rocks and adjust for features of interest. Remember that the printed image of the slide should be at the same magnification that you will use to “see” the minerals on the SEM. In order to find the selected area on the SEM, the area should be marked with dots from a black “Sharpie” pen on the carbon-coated thin section. You should make a sketch of the thin section showing the location of the selected area on the slide.

B. Backscattered Electron Image

Backscattered electrons are high energy electrons from the primary electron beam that are backscattered or repelled by the negative charges associated with the electrons of atoms comprising the mineral. The higher the electron density of the sample the greater the number of “gun” electrons that are backscattered. The higher the average atomic number of the atoms comprising the mineral the greater the electron density. The backscattered detector images these repulsed electrons.

1. Using a low magnification (~10x), locate the area of interest using the “Sharpie Dots” as a guide. With the magnification of the SEM set the same as for your optical photo, take a photo of the backscattered electron image (BSI) of the same area.

2. Describe the BSI photo of the sample or the BSI image on the monitor. Specifically, describe in what ways the BSI photo is similar to the “optical image”. Pay particular attention to the shapes, sizes and habits of the constituents.
3. Does the mosaic of constituents resemble the distribution of minerals in the “optical image” of the slide, explain.
4. Can you associate the objects in the backscattered electron image with specific minerals? How? What observations and/or properties allow you to determine this relationship?
5. How does the “backscattered electron” image differ from the “optical” image. Consider for example, color and/or brightness. Which mineral are bright and which minerals are dark. Make a list of the minerals in order of increasing brightness. What chemical property do the different bright minerals have in common? In what ways are the different darker mineral similar in composition?

C. Secondary Electron Image

Secondary electrons are the electrons from the mineral that are “knocked” off the surface of the mineral by beam electrons. Secondary electrons (SE) are imaged by a detector located above and to one side of the sample. Sample surfaces inclined toward the detector have a higher SE contrast than those surfaces inclined away from the detector. Secondary or low energy electron imaging of the surface of the sample is particularly effective for studying 3-dimensional topography at high magnification, such as in biological samples like the eye of a fly.

1. Describe the SE “picture of the sample” on the monitor. Specifically, in what ways is the image similar to the “optical” image and the “backscattered electron” image. Pay particular attention to the shapes, sizes and habits of the constituents.
2. Can you think of uses for secondary electron imaging in the study of minerals in polished thin-section? In polished thin section, the best use of the secondary electron image is to find holes in the slide, dust particles, and locate areas that are charging due to poor carbon coating. How about the study of mineral grains or powders?

D. Qualitative Chemical Analysis

In addition to being backscattered and generating secondary electrons, the BEAM electrons penetrate the mineral and displace inner shell electrons of the constituent atoms. As outer-shell electrons back-fill the inner-shell vacancies they lose energy by the emission of X-rays. The energy level (or wavelength) of the X-rays is characteristic of the element excited and the amount of energy is proportional to the number of atoms of that element in the small excitation volume. An energy dispersive X-ray spectrometer collects the X-rays for a fixed period of time (typically 30-120 seconds) at all energy levels simultaneously and an on-line computer is used to convert the data to a spectrum of X-ray intensity (“counts”) versus energy level. The resulting graph is thus a sequence of “peaks” at energy levels corresponding to specific type of atoms. The software will label the peaks with specific elements. The energy level of the K transition peaks increases with increasing atomic number so that the left to right sequence of peaks is Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe, Zn etc.

1. Now we can do some chemical petrography. Begin by obtaining a spectrum on one of the brightest minerals in the backscattered image. List the elements that make up the mineral. Suggest one or more possible identities of the mineral. How could you differentiate among these possibilities?
2. Repeat the above experiment on the other minerals in the area of interest in your slide. Can you now look at the BSI photo of the and predict the composition and name of each grain in the photo? If so why? If not, why not? Please explain.

E. Quantitative Chemical analyses

The computer has software that converts the X-ray spectrum to a quantitative analysis of the mineral by comparing the spectrum obtained from a mineral in your sample to a set of standards stored in the computer memory. This data is typically presented both as Wt% oxide and moles of atoms per formula unit of oxygen in a chemical formula such as Mg_2SiO_4 or $\text{Mg}_{0.37}\text{Fe}_{0.63}\text{SiO}_4$.

1. Determine the chemical composition of one of the minerals in the rock. How many experiments must you perform in order to do this? What are some of the reasons that the analyses are not all the "same"? When are two different analyses the same? How might you determine when two different numbers are the same or when they are different?
2. How helpful is a working knowledge of mineral compositions for using the SEM/EDS to do petrography?
3. Compare and contrast the SEM/EDS and the petrographic microscope as a tool for identifying minerals and determining the composition of the minerals. How would you tell the difference between kyanite and sillimanite - with the petrographic scope or the SEM?

COLOR IN MINERALS

M. Darby Dyar

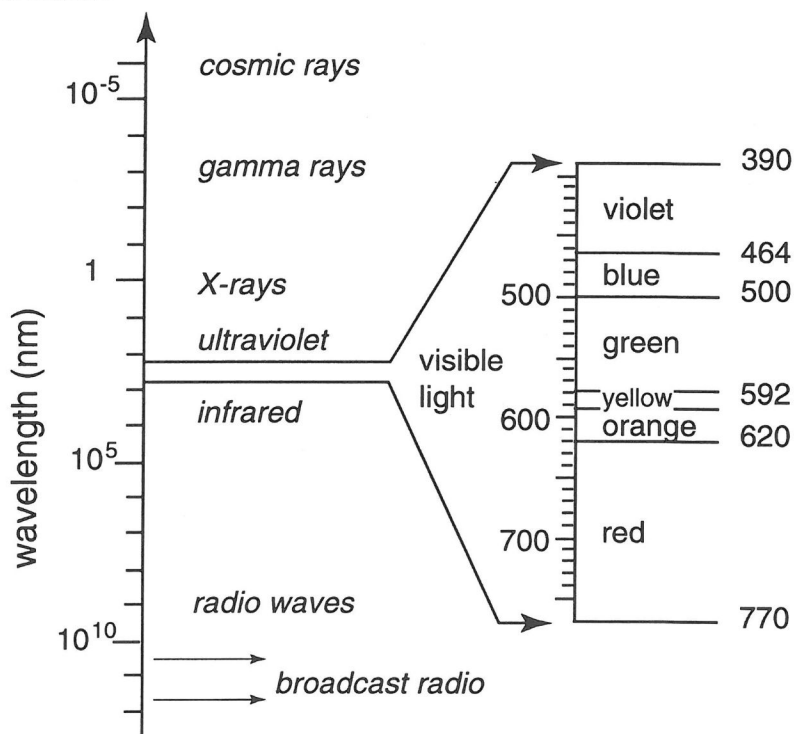
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Why do minerals have color? When is that color diagnostic, and when it is likely to fool you? Why is color important, and what can it tell us about the chemistry of minerals? Today's exercise will try to answer some of these questions, and to introduce you to the fascinating world of mineral spectroscopy, where chemistry meets mineralogy!

What is color, exactly? The color perceived by the human eye can be thought of as the sum of the wavelengths that reflect or transmit off an object, with the dominant color being the dominant wavelength of light. For the most part, color comes about through the interaction of light waves with electrons (Nassau, 1980) in a range of energies that can be perceived by the human eye. Human eyes can only distinguish about 200 gradations of color (hues) in the small region of visible light from about 400-800 nm in wavelength. Your brain creates these colors by using three sets of cones in your eyes, in the same combinations used by your television set:

black white
red green
yellow blue

Notice that the wavelengths of visible light make up only a small portion of the electromagnetic spectrum shown below.



Studies of color can often be confusing because spectroscopists use a variety of units to explain their work! These units fall into two categories: those expressed in terms of the **energy** of light (cm^{-1} , eV, and kJ) or in terms of its **wavelength** (μm , nm, or \AA). In the study of color in minerals, the two types of units most often used are wavenumbers (cm^{-1}) and wavelengths (usually expressed as nm). To convert from nm to cm^{-1} , simply take the reciprocal of nm and multiply times 10^7 . Here's a table to help you navigate between these units:

Units Used for the Study of Color

Wavelength Units		Energy Units	Resultant Color
Nanometers (nm)	Ångstroms (\AA)	Wavenumbers (cm^{-1})	
300	3,000	33,333	Ultraviolet
400	4,000	25,000	Violet
450	4,500	22,222	Blue
500	5,000	20,000	Green
550	5,500	18,182	Yellow
600	6,000	16,667	Orange
700	7,000	14,286	Red
800	8,000	12,500	Near-Infrared
900	9,000	11,111	Near-Infrared
1000	10,000	10,000	Near-Infrared
1500	15,000	6,667	Infrared
2000	20,000	5,000	Infrared
2500	25,000	4,000	Infrared

This exercise will focus on the chemistry that is responsible for making minerals (and many other things in our world) the colors that they are. Nassau (1987) describes the 15 phenomena that cause objects to have color; they are listed on the next page. Note that all but the first of these causes are created by interactions of electrons with electromagnetic radiation, usually in the central range of the electromagnetic spectrum. Fortunately, in order to understand color in minerals, we only need to examine a few of the items in Nassau's compilation. These include numbers 4, 5, 7, and 11 on the list. This lab will focus on colors caused by transition metals (4 and 5). We will learn to use mineral spectra to understand colors in minerals and gemstones, and in turn, learn to use color to help determine mineral crystal chemistry. In particular, we would like to use color (and the absorption spectra of minerals) to learn something about the valence states and coordination environments of transition metals in minerals.

Let's begin by concentrating on the transition elements. A transition element is a metal ion with a partly filled *d* or *f* shell. Generally this definition includes not only neutral ions with those characteristics, but also ions in their commonly-occurring oxidation states. The so-called first-series transition elements are those with full shells of electrons below $3f$, and incompletely full $3d$ orbitals. Another way of saying this is that they have a configuration of

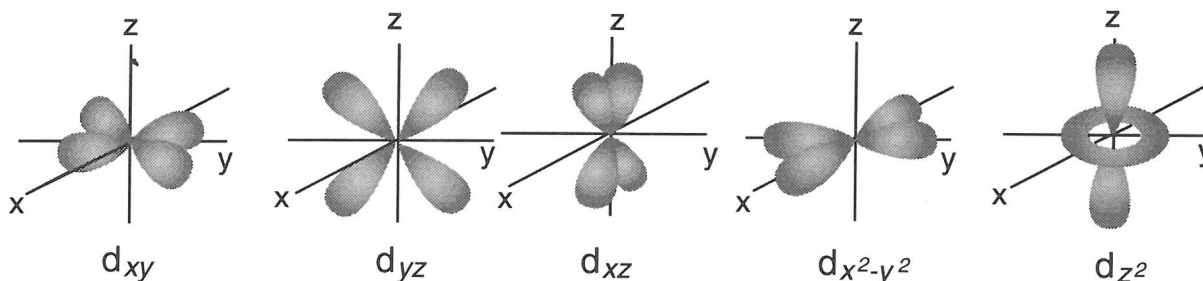
$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10-n} 4s^{1 \text{ or } 2},$$

where *n* is an integer from 0 to 10. How many electrons would an atom have in order for one or more to occupy a $3d$ orbital?

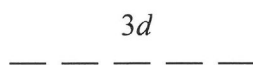
Table 1. Examples of the fifteen causes of color (adapted from Nassau, 1987)

Number	Phenomenum	Examples
1.	Incandescence (release of thermal vibration energy)	flames, lamps, carbon arc, limelight; white color of the Sun results from 5700 °C emission
2.	Gas Excitations (excitations of specific atoms)	vapor lamps, lightning, auroras, gas lasers
3.	Vibrations and Rotations (rock and roll of atoms)	blue ice, water, iodine, blue gas flame
→ 4.	Crystal Field Transitions (where chromophore ¹ is major element)	pink rhodochrosite, olivine, almandine and spessartine
→ 5.	Crystal Field Transitions (where chromophore is trace element)	ruby, emerald, chrysoberyl, rubellite, morganite
6.	Molecular Orbitals in Organics (electrons belong to several atoms)	dyes, including hair dyes and indigo blue (extracted from sea shells), bioluminescence of fireflies
→ 7.	Intervalence Charge Transfer (electrons shared by adjacent atoms)	blue sapphire, magnetite, kyanite, vivianite, aquamarine
8.	Energy Bands in Metals	copper, silver, gold, brass, iron metal
9.	Energy bands in Semiconductors	silicon, galena; zinc, cadmium, and vermilion paint pigments
10.	Doped Semiconductors	blue (B-doped) and yellow (N-doped) diamond
→ 11.	Color Centers	amethyst, smoky quartz, blue and yellow topaz, zircon, citrine
12.	Dispersive Refraction	rainbows, halos, stars in gemstones
13.	Scattering	blue sky, red sunset, blue moon, blue eyes, butterflies
14.	Interference	oil slicks, soap bubbles, coatings on camera lenses
15.	Diffraction	opal, moonstone, diffraction gratings, most liquid crystals

The 3d orbitals have the following shapes:



If an ion is *isolated* (i.e., as when floating around unbonded in outer space), all these orbitals are perfectly shaped and *have the same energy* (we call this *degenerate*). Thus, electrons filling the 3d orbitals of such an ion would have an equal probability of being located in any of them. Graphically, we illustrate this by a drawing like this:



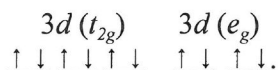
Each individual line symbolizes one of the five 3d orbitals, and all the orbital levels lie along the

¹A chromophore is an element that gives color to the material that contains it.

same horizontal line, meaning that they have the same energy.

If you look at the orbital shapes carefully, you will see that there are two distinct types of orbitals: d_{xy} , d_{yz} , and d_{xz} , collectively referred to as the t_2 or t_{2g} orbitals, and $d_{x^2-y^2}$ and d_{z^2} , collectively referred to as the e or e_g orbitals.²

In an isolated ion, a $3d$ orbital with ten electrons (all would have the same energy) would be drawn schematically like this:



Each electron is represented by an arrow; the up or down direction of the arrow indicates whether the electron is orbiting the nucleus in a clockwise or counterclockwise direction.

How would electrons be distributed among the $3d$ orbitals if there are fewer than ten of them? According to Hund's first rule, that electrons don't pair up until all the available orbitals, no matter what energy, already contain an electron. So for example, an element with five $3d$ electrons would have one electron in each orbital.

These simple, equal energy orbital configurations only work for isolated ions. What happens when a transition metal ion is incorporated into a mineral structure? You already know that most mineral structures contain cations in 4-fold, 6-fold, 8-fold, or 12-fold coordination polyhedra with oxygen as nearest neighbors. These polyhedra are sketched in the figure on the next page. It's easy to get these coordinations confused, unless you remember that the numbers refer to the number of *corners* on the polyhedra, as follows:

Terminology for Coordination Polyhedra

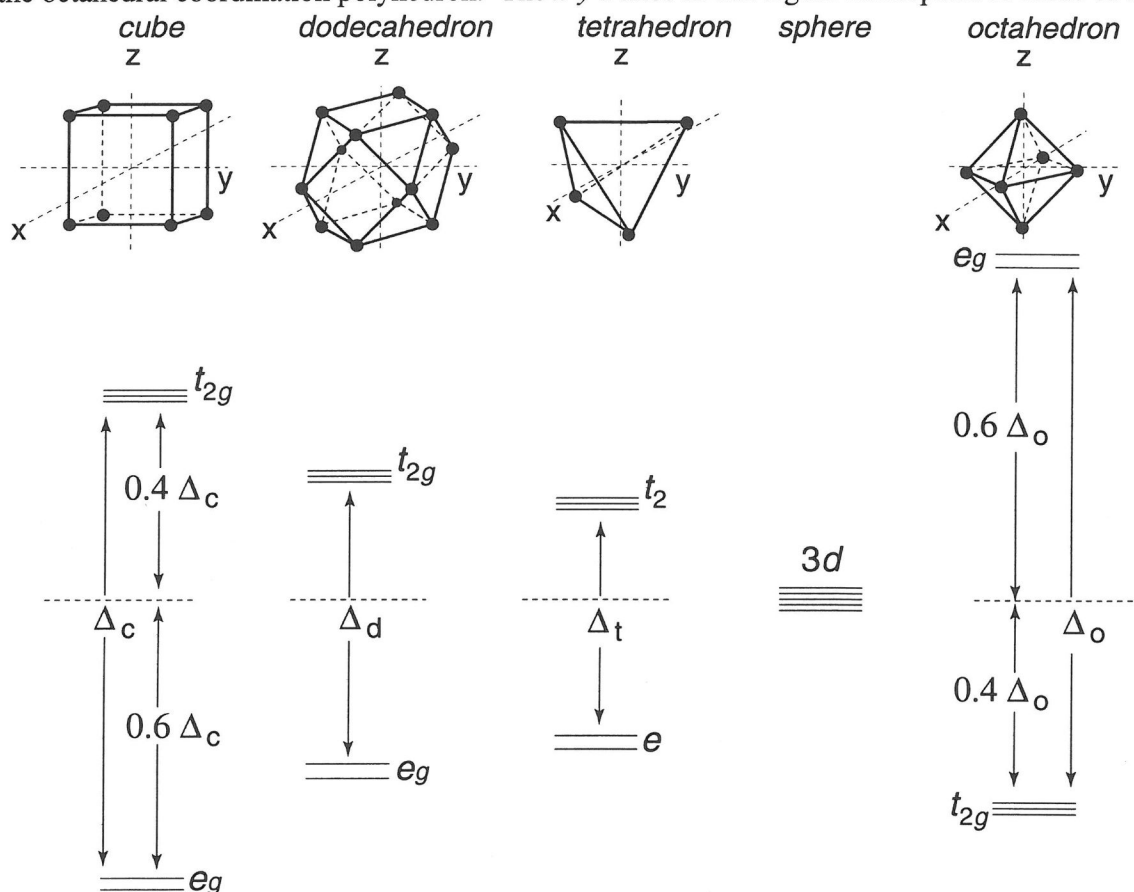
Coordination Polyhedron	Number of corners	Number of faces	Term Used	Size of Cations
tetrahedron	4	4	4-fold	smallest
octahedron	6	8	6-fold	↓
cube	8	6	8-fold	↓
dodecahedron (cuboctohedron)	12	14	12-fold	largest

The anions surrounding the transition metals in a mineral structure do not form a perfectly

²The terms t_2 , t_{2g} , e , and e_g come from group theory symmetry notation used by chemists to describe the shape of the orbitals: e means there are two orbitals per principle quantum number (so-called "two-fold degeneracy"), while t indicates three orbitals ("three-fold degeneracy"). The subscript 2 indicates that the sign of the wave function doesn't change with rotation around the axes diagonal to the Cartesian axes, and g means that the wave function does not change sign if inverted through the center of the atom. For more information, consult a chemistry text!

spherical, uniform distribution of charge around the transition metal. Instead, the charge is unevenly distributed, with negative charge being concentrated in the vicinity of the anions at the polyhedral corners. The effect of this non-spherical charge distribution is to destroy the degeneracy, which means that the energies of the orbitals are no longer all the same. Put simply, the electrons in these orbitals are repelled by the negative charge of the neighboring oxygen ions. Electrons in orbitals that are close to the oxygen neighbors are repelled more strongly than those that are further away from the oxygens. Thus the energies of the formerly equivalent $3d$ orbitals split to some with higher energies and some with lower energy levels. The total energy must stay the same.

This is shown schematically below. The degenerate energy levels for the case of an ion in a spherical field are shown in the fourth column. The small separation in the five levels is only meant to distinguish them and is not intended to imply a true energy difference. Now consider the octahedral coordination polyhedron. The x - y - z axes in this figure correspond to those of the



previous one. Thus the $d_{x^2-y^2}$ and d_{z^2} orbitals of the central transition element, which are oriented *along* the x , y , and z axes, point directly toward the neighboring oxygen ions. The repulsion raises their energy compared to the three t_{2g} orbitals, which lie *between* the axes. The sum of the energies of the five orbitals is the same as for the isolated degenerate case, so the energy of the other three orbitals must be lowered to compensate for the increase in the e_g energies.

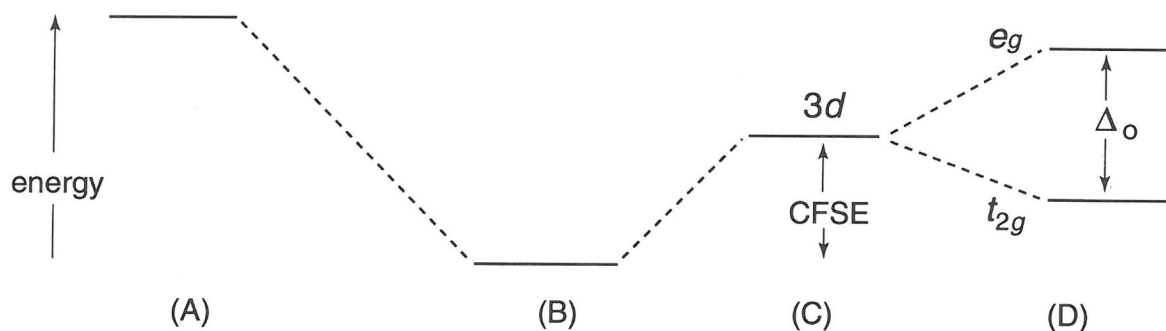
The difference in energy between the lowest orbitals and the highest orbitals is called **crystal**

field splitting and is represented by the symbol Δ (or sometimes, $10Dq$). Crystal field splitting energies are dependent on many factors, including (1) the symmetry of the coordination environment (i.e., its coordination number) as we have just learned, (2) the valence state of the cation, (3) the strength of its bond with the surrounding anions, (4) the distance between the cation and the surrounding anion, (5) pressure, and (6) temperature. Of these, (1) and (2) are extremely useful (although 3-6 also have their utilities for specific problems; see Burns' book for more information!) Many techniques for mineral analyses can tell you **what** is in your mineral, but not **where** the cations are located (i.e., what kinds of coordination polyhedra they are in) nor **which** valence states they have. For example, an electron probe analysis of a mineral might tell you that your sample contains the transition metal Fe, but it cannot tell you which sites the Fe atoms are located in, nor how much of the Fe is Fe^{3+} or Fe^{2+} . In this exercise, we will learn to use absorption spectra of minerals to tell us about the coordination number and valence state of transition metals in minerals.

You have already studied Pauling's rules and learned the usefulness of using radius ratios to predict coordination geometries of cations in minerals. Crystal field theory gives us another way to predict cation coordination, because the energies of the Δ values vary according to the coordination as seen in the figure above. This can be expressed mathematically as

$$\Delta_o : \Delta_c : \Delta_d : \Delta_t = 1 : -\frac{8}{9} : -\frac{1}{2} : -\frac{4}{9}$$

These ratios correspond to the magnitude of the splitting between t_{2g} or t_g orbitals and e_g or e orbitals. The minus sign implies that the relative stabilities of the two orbital types are reversed in the two coordinations; i.e., in octahedral coordinations, the e_g orbitals are higher energy, whereas in tetrahedral, cubic, and dodecahedral coordinations the t_{2g} orbitals are higher. **This relationship tells us that the splitting for a given transition metal will be largest when it is**



in octahedral coordination and smallest when it is in tetrahedral coordination. The Δ values obtained from real absorption spectra of minerals can be therefore be used to determine which coordination environment a transition metal is occupying.

A related concept, the **crystal field stabilization energy (CFSE)**, is derived by weighting the contributions of electrons in various orbitals. It can be thought of as the total change of energy between the perfectly symmetrical state and the coordinated state. In the diagram above

(after Burns, 1993), (A) represents the energies of the transition metal 3d orbitals in a free cation (outer space). (B) shows the energy of the orbitals once the cation is placed in a site surrounded by anions; the orbital energies decrease due to electrostatic attractions. (C) shows the change in orbital energy based on repulsion between anions and the 3d electrons in a case where the anions are distributed in a sphere. (D) shows the splitting of the 3d orbital energy levels in an octahedral crystal field.

It's actually easy to calculate CFSE, which then allows you predict which transition metals will prefer which kinds of sites in minerals. Think of CFSE as the algebraic sum of the energies of electrons in all the orbitals. Orbitals with energies that are shifted **down** as a result of crystal field splitting are considered **negative**, and orbitals that are shifted **up** are considered **positive**. For example, in octahedral coordination, each electron in a t_{2g} orbital has a lower energy than it would have in an isolated polyhedron. Therefore, every t_{2g} electron stabilizes the structure by an amount equal to $0.4 \Delta_o$. It follows that every electron in an e_g orbital would destabilize the structure by an amount equal to $0.6 \Delta_o$.³ CFSE represents the sum of the stabilizing and destabilizing effects of cations in excited and unexcited orbitals. High values for CFSE indicate that a cation is energetically preferred in a crystal site with that coordination type.

If you have actual data for $CFSE_o$ and $CFSE_t$ (see the table in your worksheet), you can calculate a parameter called Octahedral Site Preference Energy (OSPE), which is the difference between the two values. OSPE means just what it says: it's a measure of how much that cation prefers being in octahedral coordination relative to tetrahedral coordination. This allows us to make predictions about which cations might want to go into which sites in a mineral structure.

If the energies of the orbitals are split, it becomes possible for electrons to move back and forth between orbitals when energy is added (this is usually in the form of light). These transitions, of course, must be associated with energy gain or loss to the atom. Thus an electron could jump from a lower energy level to a higher one by absorbing light with an energy equal to Δ . In other words, only a very specific wavelength would be absorbed by a particular transition element in a particular site in a silicate mineral. Transition metals are particularly important in this regard, since the small energy differences between the split orbitals in certain sites often correspond to those in the visible and near-infrared region of the electromagnetic spectrum. Sunlight contains a full set of wavelengths, so it excites lots of electron jumps, causing colors in many minerals.

In the laboratory, we can measure absorption by using the relationship:

$$E = hc / \lambda$$

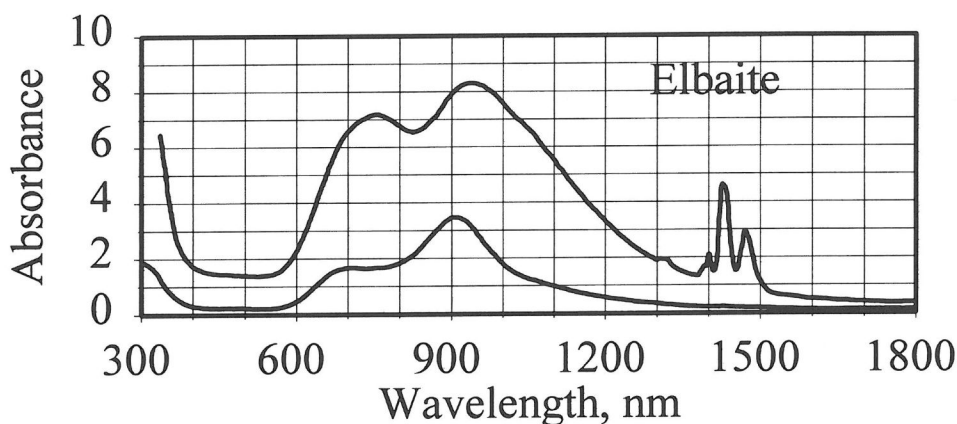
where E = energy, h = Planck's constant, c = the velocity of light, and λ = wavelength. A spectrometer passes monochromatic (single λ) light through a sample of known thickness, and

³The multiples 0.6 and 0.4 come from simple algebra: the energy of the six possible electrons in the t_{2g} orbitals ($6 \times 0.4 = 2.4$) is compensated by the energy of the four electrons in the e_g orbitals ($4 \times 0.6 = 2.4$); the total of stabilizing and destabilizing effects should be zero if all the orbitals are full!

determines the loss of intensity (absorbance) for each wavelength tested. The result is a spectrum for that mineral. The peaks in these spectra represent the wavelengths that are absorbed by the sample and the troughs correspond to the transmitted wavelengths.

The important thing for this exercise is that the value of Δ can be determined from absorption spectra of transition metal-bearing minerals because its energy generally corresponds to the visible and near-infrared region of the electromagnetic spectrum. The value of Δ is also therefore related qualitatively to the color of the mineral.

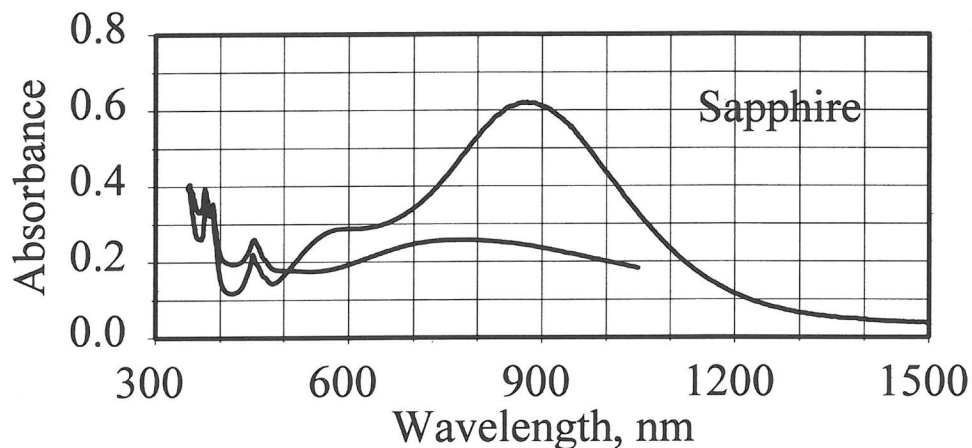
For example, here are the spectra of octahedral Cu^{2+} in elbaite, which is a kind of tourmaline. Wavelength is shown on the x axis, and the y axis shows the amount of absorbance that occurs at each wavelength. The magnitude of the absorbance is a function of the thickness of the crystal.⁴ There are two lines shown corresponding to spectra taken at two different angles to the crystal, one in which light is vibrating parallel to the c axis, and one with light vibrating perpendicular to the c axis. The two spectra are different because tourmaline is a uniaxial mineral; this means that the densities of atoms in the two orientations are different. The maximum absorption in the visible region occurs in two peaks at about $10,870\text{ cm}^{-1}$ and $14,286\text{ cm}^{-1}$, or about 920 and 700 nm. This absorption occurs in the red to infrared region of the visible light spectrum. Sunlight passing through this elbaite has its red wavelengths absorbed because they are the right energy to cause electrons to jump between split energy levels of the Cu^{2+} atoms. Light that passes through the elbaite is in the range from 400-600 nm, corresponding to blue light. Thus, this elbaite appears blue.



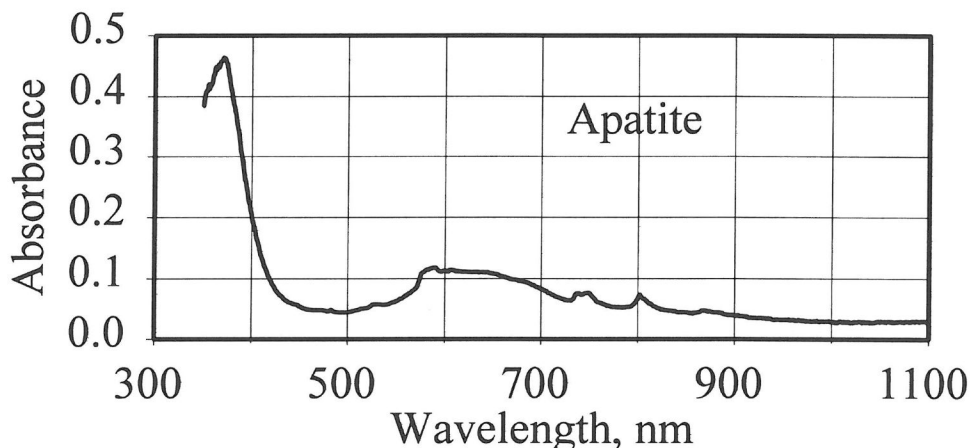
For completeness, it is worth mentioning two other causes of color in minerals (7 and 11 on Nassau's list above). Color produced by charge transfer processes is similar to crystal field-induced color, except instead of electrons jumping *between orbitals* within the same atom, electrons can jump *between atoms*. These intervalence transfers of charge can create very intense colors from very small numbers of shared electrons. In sapphire, for example, Fe^{2+} and Ti^{4+} ions in adjacent sites (ones that would normally be occupied by Al) pass an electron back

⁴In this lab exercise, absorbance is normalized so that all the spectra appear to have been measured on crystals that are 100 microns thick, in order to allow direct comparison of different spectra.

and forth. At one instant, the charge is distributed as Fe^{2+} and Ti^{4+} , and the next instant it is Fe^{3+} and Ti^{3+} . Very small amounts of Fe^{2+} and Ti^{4+} in an otherwise pure corundum crystal (Al_2O_3), even down at ppm and maybe ppb levels, can still make a sapphire blue. In the spectrum shown here, peaks at $25,680\text{ cm}^{-1}$ and $22,220\text{ cm}^{-1}$ represent Fe^{3+} and the broad bands spanning $17,800\text{ cm}^{-1}$ to $14,200\text{ cm}^{-1}$ represent intervalence charge transfer peaks.



Color can also be derived from something called a “color center” in a crystal structure. These occur when materials with otherwise perfect structures trap electrons in metastable sites. The traps can be atomic vacancies in the structure (like the electrons filling F vacancies that cause fluorite to be purple), substitutions of trace amounts of color-causing atoms for non-transition metals (as in the case of Fe^{3+} substituting for Si^{4+} in amethyst), or just locations in the crystal lattice where a minor charge deficiency provides a place for an electron to rest (as in diamond). In many cases, heat or another form of energy such as radiation can provide enough energy for an electron to “escape” from its trap, and color changes can occur. Heat and radiation treatments are frequently used in the gemstone industry to change the color of stone; for example, heat treatment can turn ugly brown zircons into gemmy blue ones. The apatite shown below has probably been heat-treated to change it from green to blue.



All of the spectra in this lab come from the Mineral Spectroscopy Home Page created by George Rossman at Caltech, which can be found at:

<http://minerals.gps.caltech.edu/>

Many of the spectra there can be downloaded and printed out as images or saved as ASCII text files. The Home Page contains a lot more information about color in minerals than can be given here. Check out your favorite mineral!

Name(s): _____

WORKSHEETS

1. Fill in the blanks to learn more about Δ_o values:

High Spin Electronic Configurations for 3d Orbitals in Octahedral Coordination

Cation	Number of 3d electrons	Electronic configuration					Unpaired electrons	CFSE
		t_{2g}					e_g	
Ca^{2+} , Sc^{3+} , Ti^{4+}	—	—	—	—	—	—	—	0
Ti^{3+}	—	—	—	—	—	—	—	$0.4 \Delta_o$
Ti^{2+} , V^{3+}	—	—	—	—	—	—	—	$— \Delta_o$
V^{2+} , Cr^{3+} , Mn^{4+}	—	—	—	—	—	—	—	$— \Delta_o$
Cr^{2+} , Mn^{3+}	—	—	—	—	—	—	—	$— \Delta_o$
Mn^{2+} , Fe^{3+}	—	—	—	—	—	—	—	$— \Delta_o$
Fe^{2+} , Co^{3+} , Ni^{4+}	—	—	—	—	—	—	—	$— \Delta_o$
Co^{2+} , Ni^{3+}	7	<u>↑↓</u>	<u>↑↓</u>	<u>↑</u>	<u>↑</u>	<u>↑</u>	3	Δ_o
Ni^{2+}	—	—	—	—	—	—	—	$1.2 \Delta_o$
Cu^{2+}	—	—	—	—	—	—	—	$— \Delta_o$
Cu^+ , Zn^{2+} , Ga^{3+} , Ge^{4+}	—	—	—	—	—	—	—	$— \Delta_o$

Reminder: to calculate CFSE, assign a weight of 0.4Δ for each electron that occupies a t_{2g} or t_2 orbital, and 0.6Δ for each electron in an e_g or e orbital; assign a positive charge to the electrons in lower (stabilizing) energy orbitals and a negative charge to those in higher (destabilizing) energy orbitals. When you sum up these contributions (write the sum in the right-hand column of each table), you get the net stabilization energy (CFSE) of each transition metal.

The table above gives the predicted CFSE for the various cations, but it is expressed in terms of a fraction multiple of Δ_o . Experimental data on Δ_o are then used to estimate an actual value for CFSE. In the following table (values from Table 2.5 in Burns, 1993), we explore the relationships between these variables.

Relationship Between Crystal Field Splittings and CFSE for Octahedral Coordination

Cation	Δ_o (cm^{-1})	CFSE (right column, above)	CFSE (cm^{-1}) in hexahydrate
Ti^{3+}	_____	$— \Delta_o$	7,580
V^{3+}	_____	$— \Delta_o$	15,280
V^{2+}	12,600	$— \Delta_o$	15,120

Cr ³⁺	_____	_____ Δ_o	20,880
Cr ²⁺	_____	_____ Δ_o	8,340
Mn ³⁺	_____	_____ Δ_o	12,600
Mn ²⁺	7,800	_____ Δ_o	0
Fe ³⁺	13,700	_____ Δ_o	0
Fe ²⁺	_____	_____ Δ_o	3,760
Co ²⁺	_____	_____ Δ_o	7,440
Ni ²⁺	_____	_____ Δ_o	10,200
Cu ²⁺	_____	_____ Δ_o	7,800

From this table you can generate a general sequence of Δ_o values, which illustrates some of the general trends in Δ_o :

$$\text{Mn}^{2+} < ______ < ______ < ______ < ______ < ______ < ______ < ______ < ______ < ______ < \text{Mn}^{3+}$$

From this list, what can you conclude about the values of Δ_o for trivalent cations relative to the corresponding divalent ions? (Pick one!)

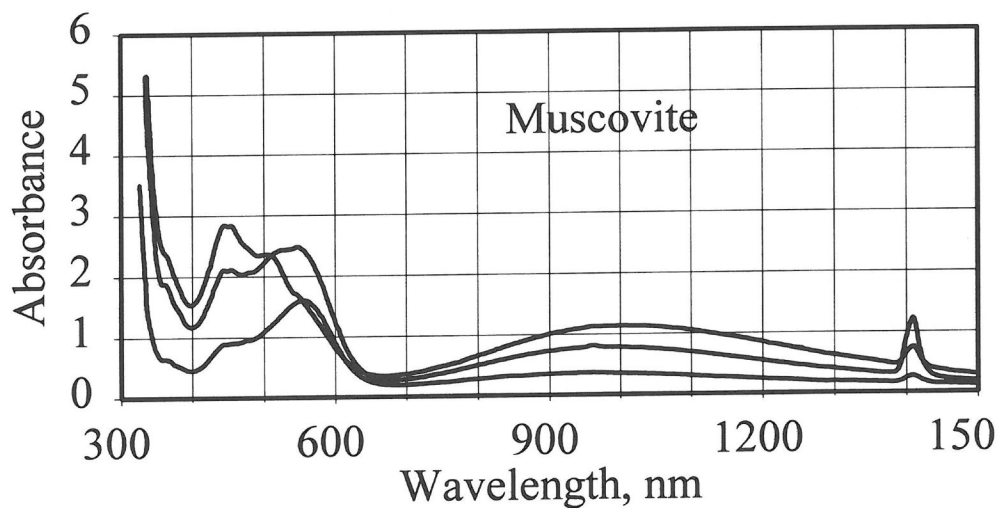
$$\Delta^{3+} > \Delta^{2+}$$

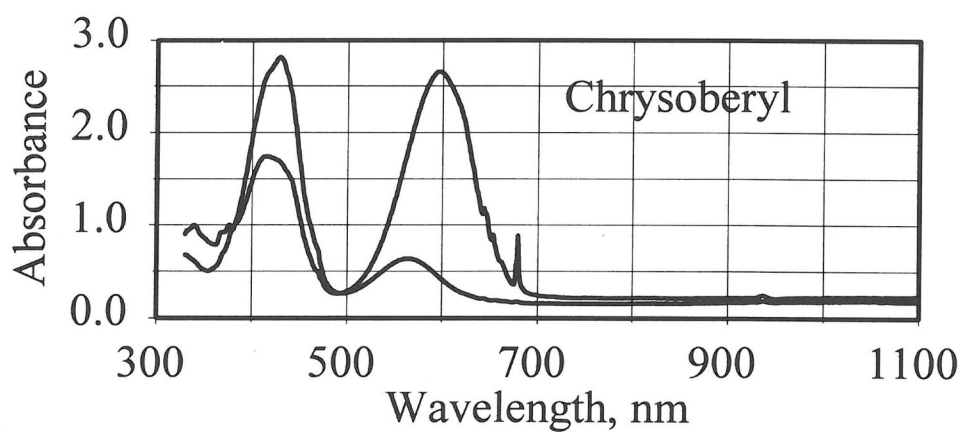
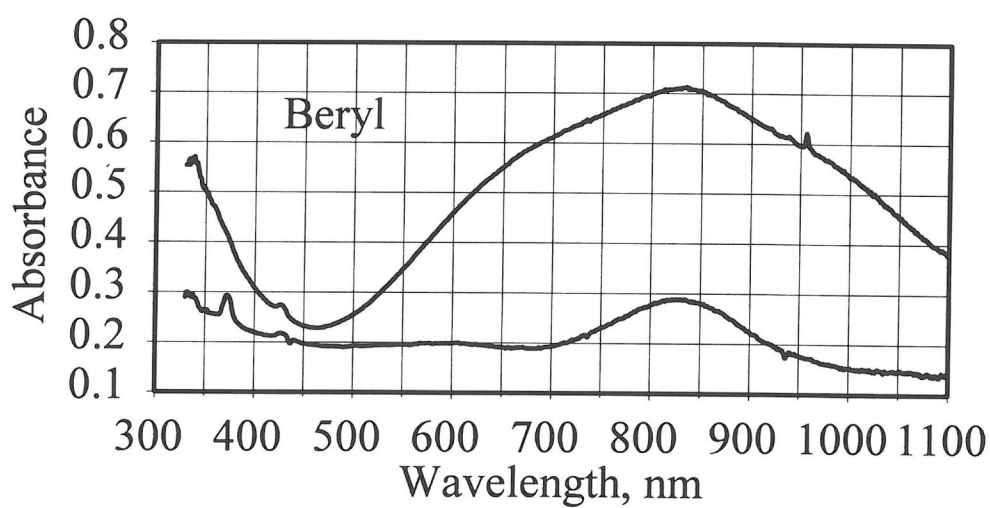
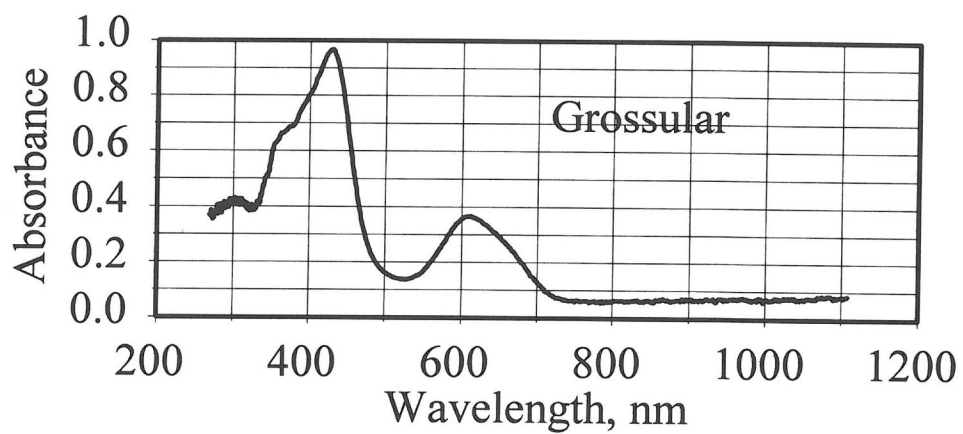
OR

$$\Delta^{3+} < \Delta^{2+}$$

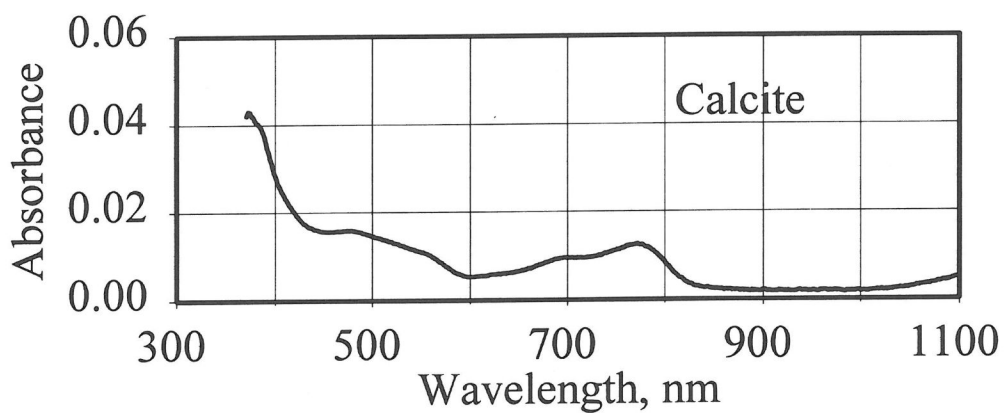
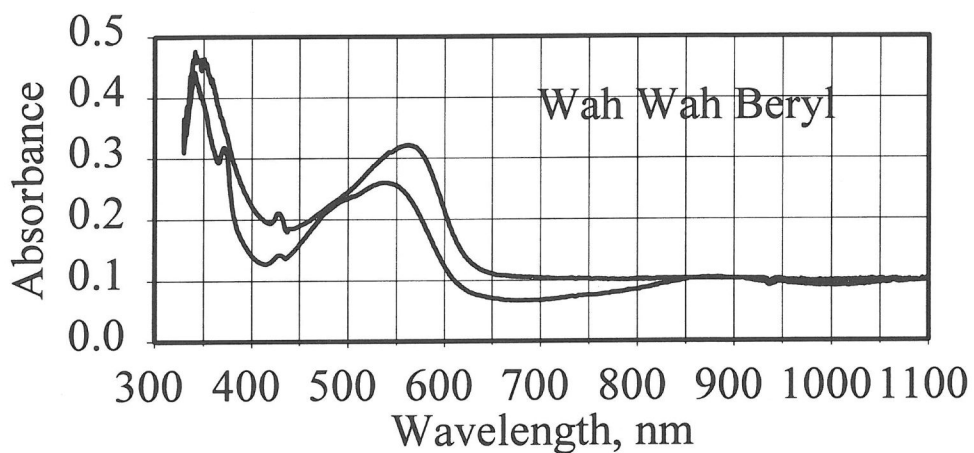
HINT: you will use this relationship to help you interpret the spectra in question #3!

2. Mystery Minerals: What color am I? For each of the spectra given below, identify the region of minimum absorption, where light is NOT being absorbed and decide what color this mineral might be! Warning: some of these minerals have unusual colors!

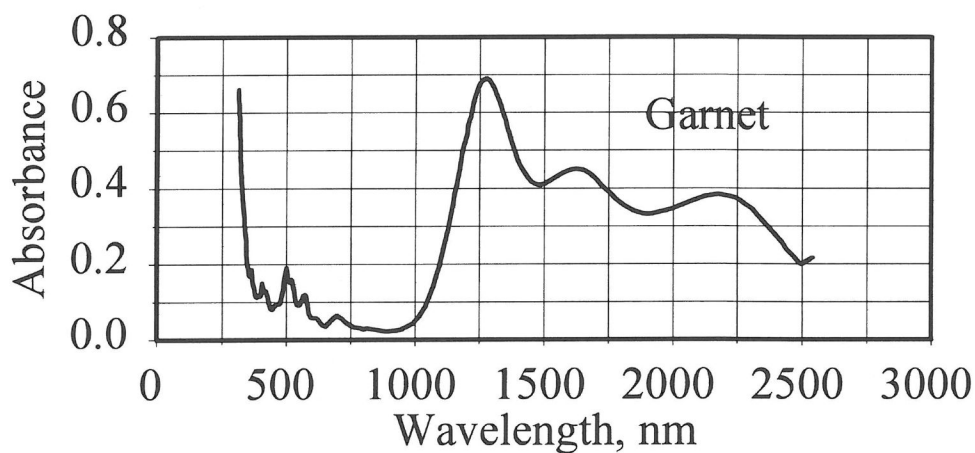
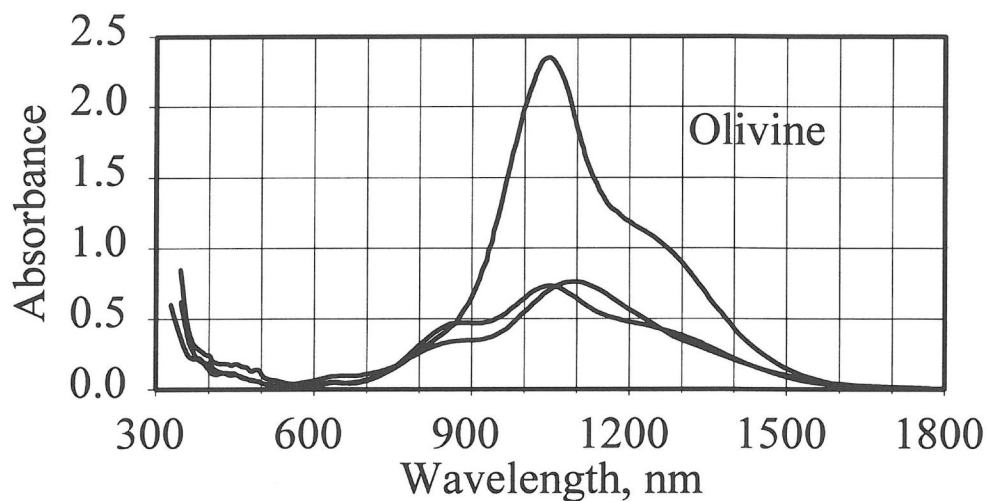




3. Earlier in this exercise, we pointed out that one of the best uses for crystal field theory is to help distinguish between multiple valence states of the same element. Two spectra containing the element Mn are shown below. One contains Mn^{3+} and the other Mn^{2+} . First, determine the maximum absorption in each and convert it to wavenumbers. Then, use the order of Δ_o values you determined in question #1 to determine which mineral contains which valence of Mn.



4. Below you will find spectra of Fe^{2+} in two minerals, fayalite (Fe-rich olivine) and pyrope (Mn- and Fe-rich garnet). Determine the energy (in wavenumbers) of the most intense absorption peak in each spectrum, and decide which one has Fe^{2+} in octahedral coordination, and which in eight-fold coordination. Compare this to the minerals staurolite and spinel, in which Fe^{2+} has maximum absorbance at around 1400-2200 nm and 2070 nm, respectively. What type of coordination environment do you think the Fe^{2+} occupies in these minerals, and why?



5. Crystal field theory is useful not just for understanding color, but for understanding why different elements occupy different sites in minerals. Calculate the CFSE values for cations in tetrahedral coordination.

High Spin Electronic Configurations for 3d Orbitals in Tetrahedral Coordination

Cation	Number of 3d electrons	Electronic configuration					Unpaired electrons	CFSE
		<i>e</i>		<i>t₂</i>				
Ca ²⁺ , Sc ³⁺ , Ti ⁴⁺	—	—	—	—	—	—	—	0
Ti ³⁺	—	—	—	—	—	—	—	0.6 Δ _t
Ti ²⁺ , V ³⁺	—	—	—	—	—	—	—	—Δ _t
V ²⁺ , Cr ³⁺ , Mn ⁴⁺	—	—	—	—	—	—	—	—Δ _t
Cr ²⁺ , Mn ³⁺	—	—	—	—	—	—	—	—Δ _t
Mn ²⁺ , Fe ³⁺	—	—	—	—	—	—	—	0 Δ _t
Fe ²⁺ , Co ³⁺ , Ni ⁴⁺	—	<u>↑↓</u>	<u>↑</u>	<u>↑</u>	<u>↑</u>	<u>↑</u>	4	—Δ _t
Co ²⁺ , Ni ³⁺	—	—	—	—	—	—	—	—Δ _t
Ni ²⁺	—	—	—	—	—	—	—	0.8 Δ _t
Cu ²⁺	—	—	—	—	—	—	—	—Δ _t
Cu ⁺ , Zn ²⁺ , Ga ³⁺ , Ge ⁴⁺	—	—	—	—	—	—	—	—Δ _t

Now, use the difference between CFSE_o and CFSE_t to calculate octahedra site preference energy, or OSPE. Note that this assumes that all the coordination polyhedra are regular and undistorted in shape. Real data from papers by McClure (1957) and Dunitz and Orgel (1957) are given below for transition metals in oxides structures (after Burns, 1993).

Note: you can also do a similar type of calculation for preferences of cations for, say, octahedral vs. dodecahedral sites. But this is the one with the most utility, however, because most sites for transition metals in minerals are either tetrahedral or octahedral.

Octahedral Site Preference Energies of Transition Metals

Cation	CFSE _o (Kj/mole)	CFSE _t (Kj/mole)	OSPE (Kj/mole)
Ca ²⁺ , Sc ³⁺ , Ti ⁴⁺	0	0	0
Ti ³⁺	-87.4	-58.6	-28.8
V ³⁺	-160.2	-106.7	—
Cr ³⁺	-224.7	-66.9	—
Cr ²⁺	-100.4	-29.3	—
Mn ³⁺	-135.6	-40.2	—

Mn ²⁺ , Fe ³⁺	0	0	0
Fe ²⁺	-49.8	-33.1	_____
Co ³⁺	-188.3	-108.8	_____
Co ²⁺	-92.9	-61.9	_____
Ni ²⁺	-122.2	-36.0	-86.2
Cu ²⁺	-90.4	-26.8	_____
Zn ²⁺ , Ga ³⁺ , Ge ⁴⁺	0	0	0

For divalent cations, the order of OSPE is:

Ni²⁺ > _____ > _____ > _____ > _____ > _____ = _____ = _____

For trivalent cations, the order of OSPE is:

Cr³⁺ > _____ > _____ > _____ > _____ > _____ = _____ = _____

Therefore, if you are crystallizing a mineral (say, a spinel) with both octahedral and tetrahedral sites in it, and you have Cu²⁺, Cr³⁺, and Ti³⁺, you might predict that the Cu²⁺ and Cr³⁺ would prefer octahedral sites, and the Ti³⁺ wouldn't mind occupying tetrahedral sites. It turns out that this theory does accurately predict many observed mineral structures. It can also be used to predict the order by which cations will prefer to leave a melt (where metals are predominantly tetrahedrally coordinated) and enter minerals such as olivine (where they can exist in octahedral coordination).

COLOR IN MINERALS

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INTRODUCTION AND INSTRUCTOR'S NOTES

This lab exercise is adapted from one I've developed over the years to teach crystal field theory to students in my Geochemistry courses. I must confess that although my own research interests lie in this area (I had the good fortune to work with both Roger Burns and George Rossman), I have never included spectroscopy as part of my own Mineralogy courses. Why? ...because I did not think I could present it in a fashion that would make it interesting and relevant to my students without oversimplification. Now that George Rossman has a home page with easily accessible spectra and images, I've changed my mind. In preparing for this workshop, I've also reflected on the fact that the students I've had in Mineralogy are almost universally interested in gemstones, and by association, in their colors. I've tried to write this lab exercise to take advantage of that interest.

Unfortunately, most Geology departments do not have the equipment to make measurements of optical spectra in house. If you do, I encourage you to change this lab around so that the students actually take some spectra themselves. Sample preparation requires only that you have a slice of the mineral that is polished on both sides, a relatively easy undertaking with some elbow grease, a little diamond grit, and a polishing setup. If you lack the spectrometer, this "lab" becomes more of an exercise. To add a little "hands-on" work to it, you might consider pulling colored specimens from your own collections, and then ask the students to match spectra with samples. This reinforces the relationship between how the spectra look and how the colors actually appear. A visit to or from a local jeweler (look for someone with Gemological Institute of America certification) might also give you a chance to see some nice colored gems; most jewelers today also stock treated and untreated stones, which your students might want to see.

I also encourage you to take advantage of George Rossman's Mineral Spectroscopy Home Page (see information below), to which new spectra are constantly being added. Take a look at it from time to time; new updates will be added that will also stimulate good discussions of spectroscopy. Most of the entries for mineral spectra contain brief discussions of the causes of color that are applicable. You might want to ask your students to download and manipulate the spectra. The data files all contain information about the thickness of each sample when it was run; you could ask your students to download some spectra, normalize them all to the same thickness, and talk about the Beer-Lambert law and the relationship between absorption and concentration.

Finally, I encourage you to contact me (mddyar@amherst.edu) or George Rossman (see his home page for information on how to reach him) if you have questions about the subject matter presented here. I hope that some of my own enthusiasm for this subject matter and this lab will prove contagious, and inspire you to work with your students on this topic. Really, your imagination is the only limit to the interesting ways to present mineral spectra!

SHOW AND TELL

All of the spectra in this lab come from the Mineral Spectroscopy Home Page created by George Rossman at Caltech, which can be found at:

<http://minerals.gps.caltech.edu/>

We all owe George a huge debt of thanks for creating this facility, and I am particularly grateful that he allowed us to use the spectra in this exercise. Many of the spectra can be downloaded and printed out as images or saved as ASCII text files. This gives you an opportunity to go beyond the lab ideas presented here into territory of particular interest to you or your students.

BACKGROUND

I would insert this lab at the point in my course where I have completed the study of symmetry and want to begin basic mineral chemistry. I talk very briefly about atoms (what's a neutron, proton, electron; what are the symbols for them; charge neutrality) and then present the Schrödinger equation as a way of constructing the periodic chart. I stress that it also describes the positions of electrons in space around the nucleus, and I use some wood models to show them the shape of the orbitals. We then break into groups and run through the following exercise (it takes 30-45 minutes) to get them used to thinking about the periodic chart:

Periodic Chart Exercise

1. Use the periodic chart to decide what characterizes each of the following:

- A: Transition elements (e.g., Sc through Zn; also Y through Cd)
 - B: Lanthanides (Ce through 72)
 - C: Actinides (Th through Lr)
 - D: Alkali Metals (e.g., Li, Na, K, Rb)
 - E: Alkaline Earths (e.g., Be, Mg, Ca)
 - F: Halogens (F, Cl, Br, I)
 - G: Noble Gases (He, Ne, Ar)
 - H: Platinum Group Elements (e.g., Ru, Os, Rh)
-

2. Calculate the atomic weight of Mg_2SiO_4 .

Depending on the preparation of my students, sometimes I also have the class do an exercise predicting which valences each atom likes to take on, with emphasis on rock-forming elements. At this point it is also convenient to talk about ionic radius, emphasizing the fact that atoms have different radii in different coordinations with oxygen (John Brady has an excellent lab exercise on how ionic radii can be determined!) Pauling's Rules (with corollaries) and Hund's rules are also important background for this exercise.

Once the class seems comfortable with these fundamentals of chemistry, they are ready to tackle color in minerals. The materials included here may cover one or two lab periods depending on your student population. The only materials needed would be a periodic chart of

the elements and, perhaps, wood models of the shapes of the *d* orbitals to aid in understanding the crystal field theory. It's also nice to have examples of minerals of different color (only be sure you know why each one is colored the way it is -- the students are bound to ask!) If you can gather them together, it's particularly nice to have examples of something close to the six garnet end members (for obvious reasons).

I've included far more questions here than can be dealt with in a single lab period, but I am hopeful that you will choose the parts of this document that seem interesting and use them in any way you want. To help you do this, I've assembled the following table with a guide to some of the spectra that appear on the Mineral Spectroscopy Home Page, along with some references to get you started. Many other references are given in the list on the Home Page. I hope you find this useful...

Summary of Some of the Mineral Spectra Available on the Home Page

Mineral	Peak Position (nm)	Peak positions (cm ⁻¹)	Color	Assignment	Relevant references
ruby	556 408	18,000 24,500	red	Cr ³⁺ (oct)	Burns, 1983
beryl (Lone P.)	820 971	12,200 10,300	blue	Fe ²⁺ (oct)	Rossman's home page
beryl (WahWah)	621 556-500	16,100 18,000-20,000	red	Mn ³⁺ (oct)	Rossman's home page
beryl (syn. em.)	620 425	16,130 23,530	green	Cr ³⁺ (oct)	Rossman's home page
almandine	505 574 694 1309 1718	19,800 17,430 14,400 7,640 5,820	red	Fe ²⁺ (8-fold)	Burns, 1993
andradite	854 588 441-437	11,700 17,000 22,670-22,900	green	Fe ³⁺ in M3 (oct)	Moore and White, 1972
grossular	607 426	16,475 23,475	green	V ³⁺ (oct)	Rossman, 1988
pyrope	500 530 610 700	20,000 18,868 16,393 14,286	red/pink	Fe ²⁺ (8-fold)	Burns, 1993
spessartine	588 490	17,000 20,400	orange	Mn ²⁺ (oct)	Freundrup and Larger, 1981
uvarovite	600 440	16,667 22,727	green	Cr ³⁺ (oct)	Abu-Eid, 1976
sillimanite	462 440 412	21,645 22,727 24,272	yellow	Fe ³⁺ (tet)	Rossman's home page
fayalite	1076 909 1250	9,290 11,000 8,000	green	Fe ²⁺ (oct)	Burns, 1970
manganite	580 500	17,240 20,000	red	Mn ³⁺ (oct)	Rossman's home page

gahnite	450	22,222	???	Zn ²⁺ (tet)	Rossman's home page
	540	18,519			
	570	17,544			
	630	15,873			
	900	11,111			
spinel	400	25,000	red	Cr ³⁺ (oct)	Mao and Bell, 1975
	570	17,544			
chrysoberyl	565	17,700	green	Cr ³⁺ (oct)	Farrell and Newnham, 1965
(Kenya)	425	23,500			Schmetzer et al., 1980
chrysoberyl	375	26,600	yellow	Fe ³⁺ (oct)	Rossman's home page
(M.G.)	440	22,727			
grunerite	1000	10,000	blue	Fe ²⁺ in M4 (oct)	Mao and Seifert, 1974 Hawthorne, 1981
	2336	4,200		" "	
	990	10,100		Fe ²⁺ in M1-M3 (oct)	
	1176	8,500		" "	
phlogopite	840	11,900	green	Fe ²⁺ (oct)	Rossman, 1984
(Ontario)	1124	8,900			
phlogopite	521	19,200	red	Fe ³⁺ (tet)	Faye and Hogarth, 1969
(Kimberley)	493	20,300			Hogarth et al., 1970
	441	22,700			
	400	25,000			
muscovite	673	14,850	red	Mn ³⁺ (dist. oct)	Burns, 1970
	525	19,050			
	467	21,400			
	420	23,800			
lepidolite	758	13,200	pink	Mn ³⁺ (dist. oct)	Annersten and Hålenius, 1976
	548	18,250			
	458	21,850			
epidote	1056-769	9,470-12,300	green	M3 (oct) Fe ³⁺	Burns and Strens, 1967
	607-559	16,480-17,900			
	472-455	21,200-22,000			

READING LIST

The technical literature contains a wide variety of papers covering gems, color, and optical spectroscopy; projects on color in minerals make good term paper topics once students have gotten used to interpreting optical spectra of minerals. The majority of the recent work in this area has been done at Caltech, so searches of literature databases using George R. Rossman as author as a search criterion will yield a good starting point for such papers. I also recommend the *Reviews in Mineralogy* volume on *Spectroscopy* (F.W. Hawthorne, ed.), which has a good chapter in it (by Rossman) summarizing optical spectroscopy. The "bible" of this field is Roger Burns' book, *Mineralogical Applications of Crystal Field Theory* (1970 and 1993; Cambridge University Press). Despite the somewhat intimidating title, it contains clear explanations of all the material presented in this lab, along with data on just about every mineral group you could ever want to know about!

If you're not too familiar with this material yourself, you might want to begin with less specialized reading material. I highly recommend the following readings, which you might want to have available for eager-beaver students. Some of these papers are rather old now, but they are still (in my opinion) the best that have been written on this topic.

and to George Rossman for perennial wisdom on this subject and for helping out with a few last minute spectra. I am also grateful for all that I learned from Roger Burns and from his book.

ANSWERS TO PROBLEMS

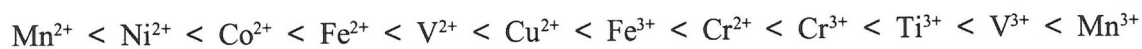
High-Spin Electronic Configurations for 3d Orbitals in Octahedral Coordination

Cation	Number of 3d electrons	Electronic configuration					Unpaired electrons	CFSE
		t_{2g}	e_g					
Ca ²⁺ , Sc ³⁺ , Ti ⁴⁺	0						0	0
Ti ³⁺	1	↑					1	0.4 Δ _o
Ti ²⁺ , V ³⁺	2	↑	↑				2	0.8 Δ _o
V ²⁺ , Cr ³⁺ , Mn ⁴⁺	3	↑	↑	↑			3	1.2 Δ _o
Cr ²⁺ , Mn ³⁺	4	↑	↑	↑	↑		4	0.6 Δ _o
Mn ²⁺ , Fe ³⁺	5	↑	↑	↑	↑	↑	5	0
Fe ²⁺ , Co ³⁺ , Ni ⁴⁺	6	↑↓	↑	↑	↑	↑	4	0.4 Δ _o
Co ²⁺ , Ni ³⁺	7	↑↓	↑↓	↑	↑	↑	3	0.8 Δ _o
Ni ²⁺	8	↑↓	↑↓	↑↓	↑	↑	2	1.2 Δ _o
Cu ²⁺	9	↑↓	↑↓	↑↓	↑↓	↑	1	0.6 Δ _o
Cu ⁺ , Zn ²⁺ , Ga ³⁺ , Ge ⁴⁺	10	↑↓	↑↓	↑↓	↑↓	↑↓	0	0

Relationship Between Crystal Field Splittings and CFSE for Octahedral Coordination

Cation	Δ _o (cm ⁻¹)	CFSE (right column, above)	CFSE (cm ⁻¹) in hexahydrate
Ti ³⁺	18,950	0.4 Δ _o	7,580
V ³⁺	19,100	0.8 Δ _o	15,280
V ²⁺	12,600	1.2 Δ _o	15,120
Cr ³⁺	17,400	1.2 Δ _o	20,880
Cr ²⁺	13,900	0.6 Δ _o	8,340
Mn ³⁺	21,000	0.6 Δ _o	12,600
Mn ²⁺	7,800	0.0 Δ _o	0
Fe ³⁺	13,700	0.0 Δ _o	0
Fe ²⁺	9,400	0.4 Δ _o	3,760
Co ²⁺	9,300	0.8 Δ _o	7,440
Ni ²⁺	8,500	1.2 Δ _o	10,200
Cu ²⁺	13,000	0.6 Δ _o	7,800

It follows that:



From this list it is obvious that $\Delta^{3+} > \Delta^{2+}$ is the general rule! For more information consult section 2.9 in Burns (1993).

2. Mystery minerals:

Before you do this section, remind the students of where the infrared portion of the spectrum is, and ask them if their eyes can see infrared light! This will avoid confusion over minima that occur in the IR that don't affect color. For more information on these spectra,

consult the summary table of mineral spectra for more information, or check out the Mineral Spectroscopy Home Page. There are lots of other good examples there that can be used for this type of question.

Minas Gerais **muscovite** is red-purple (Mn^{3+}).

Grossular is green (V^{3+}).

Beryl is blue (Fe^{2+}).

Chrysoberyl is green, with flashes of red (this is called the “alexandrite effect”), because it has low absorption in both the green and the red regions of the spectrum. Chrysoberyl appears green in daylight and red in incandescent light. This occurs because in daylight, red and green are transmitted equally, but the eye is more sensitive to green, so it appears green. Incandescent light happens to be enriched in low energy red wavelengths, so alexandrite transmits more red than green and it appears red!

3. The Wah Wah beryl has maximum absorbance at 550-580 nm. In wavenumbers this is 18,182 - 17,241 cm^{-1} . The calcite, on the other hand, has maximum absorption at about 780 nm, or 12,821 cm^{-1} . Because the general rule from #1 is that $\Delta^{3+} > \Delta^{2+}$, the beryl must be the Mn^{3+} , while the calcite is Mn^{2+} .

4. Olivine has maximum absorption at about 1100 nm, or 9,091 cm^{-1} , while the pyrope has a maximum at around 1260 nm (7,937 cm^{-1}). Theory predicts that $\Delta_o : \Delta_t = 1 : 8/9$, so the garnet has the Fe in eight-fold coordination, while the olivine is six-fold. In staurolite and spinel, with maximum absorbances around 1400-2200 nm (7143-4545 cm^{-1}) and 2070 nm (4831 cm^{-1}), the energies are roughly 4/9 of the value for octahedral Fe^{2+} (as in olivine), so the Fe^{2+} in those minerals is in tetrahedral coordination.

5.

High Spin Electronic Configurations for 3d Orbitals in Tetrahedral Coordination

Cation	Number of 3d electrons	Electronic configuration					Unpaired electrons	CFSE
		<i>e</i>			<i>t</i> ₂			
Ca^{2+} , Sc^{3+} , Ti^{4+}	0						0	0
Ti^{3+}	1	↑					1	0.6 Δ_t
Ti^{2+} , V^{3+}	2	↑	↑				2	1.2 Δ_t
V^{2+} , Cr^{3+} , Mn^{4+}	3	↑	↑	↑			3	0.8 Δ_t
Cr^{2+} , Mn^{3+}	4	↑	↑	↑	↑		4	0.4 Δ_t
Mn^{2+} , Fe^{3+}	5	↑	↑	↑	↑	↑	5	0
Fe^{2+} , Co^{3+} , Ni^{4+}	6	↑↓	↑	↑	↑	↑	4	0.6 Δ_t
Co^{2+} , Ni^{3+}	7	↑↓	↑↓	↑	↑	↑	3	1.2 Δ_t
Ni^{2+}	8	↑↓	↑↓	↑↓	↑	↑	2	0.8 Δ_t
Cu^{2+}	9	↑↓	↑↓	↑↓	↑↓	↑	1	0.4 Δ_t
Cu^+ , Zn^{2+} , Ga^{3+} , Ge^{4+}	10	↑↓	↑↓	↑↓	↑↓	↑↓	0	0

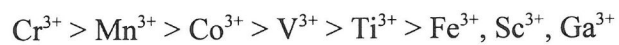
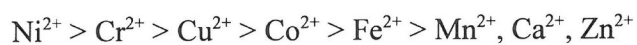
In case you're wondering, most cations in the first transition series have high spin configurations at ambient pressure and temperature. The exceptions to this are Co^{3+} and Ni^{3+} , but for simplicity, only high spin configurations are used in this lab exercise. For more

information on high spin vs. low spin, see Burns (1993) or a chemistry text.

Octahedral Site Preference Energies of Transition Metals

Cation	CFSE _o (Kj/mole)	CFSE _t (Kj/mole)	OSPE (Kj/mole)
Ca ²⁺ , Sc ³⁺ , Ti ⁴⁺	0	0	0
Ti ³⁺	-87.4	-58.6	-28.8
V ³⁺	-160.2	-106.7	-53.5
Cr ³⁺	-224.7	-66.9	-157.8
Cr ²⁺	-100.4	-29.3	-71.1
Mn ³⁺	-135.6	-40.2	-95.4
Mn ²⁺ , Fe ³⁺	0	0	0
Fe ²⁺	-49.8	-33.1	-16.7
Co ³⁺	-188.3	-108.8	-79.5
Co ²⁺	-92.9	-61.9	-31.0
Ni ²⁺	-122.2	-36.0	-86.2
Cu ²⁺	-90.4	-26.8	-63.7
Zn ²⁺ , Ga ³⁺ , Ge ⁴⁺	0	0	0

These would predict the following uptake systematics:



BETTER LIVING THROUGH MINERALS X-RAY DIFFRACTION OF HOUSEHOLD PRODUCTS

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(with apologies and thanks to Mike Holdaway)

As you have learned in lecture, X-ray diffraction is a quick and valuable tool for identifying minerals. Minerals are an integral portion of our everyday life, in addition to composing our planet! They help bring electricity into our homes and remove our bathtub rings.

In this lab you will analyze the X-ray diffraction patterns of three household cleansers, *Ajax*, *White Magic*, and *Soft Scrub*, in order to identify the abrasive minerals in each. Haven't you wondered what puts the "soft" in *Soft Scrub*?

The diffraction patterns for the three samples are photocopied for you as the last three pages of this lab. These samples were run without using an internal standard so any peak shifts remain uncorrected relative to their ideal positions. This, combined with errors in hand measurement of peak positions, produce errors in your calculated d-values. Consequently, 2θ angles which have been corrected using a corundum standard are also provided.

ASSIGNMENT

1. Measure the 2θ angles for the peaks of the abrasive minerals from the diffraction patterns for each of the three cleansers. For each pattern, list the angles in order of decreasing intensity in the space provided.
2. Compare your measured 2θ angles to those values listed in the second column. These 2θ angles have been corrected using a corundum standard.
3. Calculate the corresponding d-values for each peak using the Bragg equation:

$$n\lambda = 2d \sin \theta$$
$$\lambda = 1.5405 \text{ \AA} \text{ (Cu K}_{\alpha} \text{ X-ray wavelength)}$$

4. Match the sets of d-values to those in the table of d-values for common, light-colored minerals (found on the last page) to identify the abrasive mineral in each sample.
5. Answer the questions at the end of the lab.

Sample 1: **White Magic**

Mineral: _____

2θ measured	2θ ideal	d-values measured	d-values ideal
.....	31.20
.....	51.50
.....	50.95
.....	41.56
.....	45.21

Sample 2: **Ajax**

Mineral: _____

2θ measured	2θ ideal	d-values measured	d-values ideal
.....	26.71
.....	21.03
.....	36.50
.....	50.18
.....	40.35
.....	60.04

Sample 3: **Soft Scrub**

Mineral: _____

2θ measured	2θ ideal	d-values measured	d-values ideal
.....	29.80
.....	47.79
.....	48.80
.....	39.65
.....	43.50
.....	57.75
.....	23.30

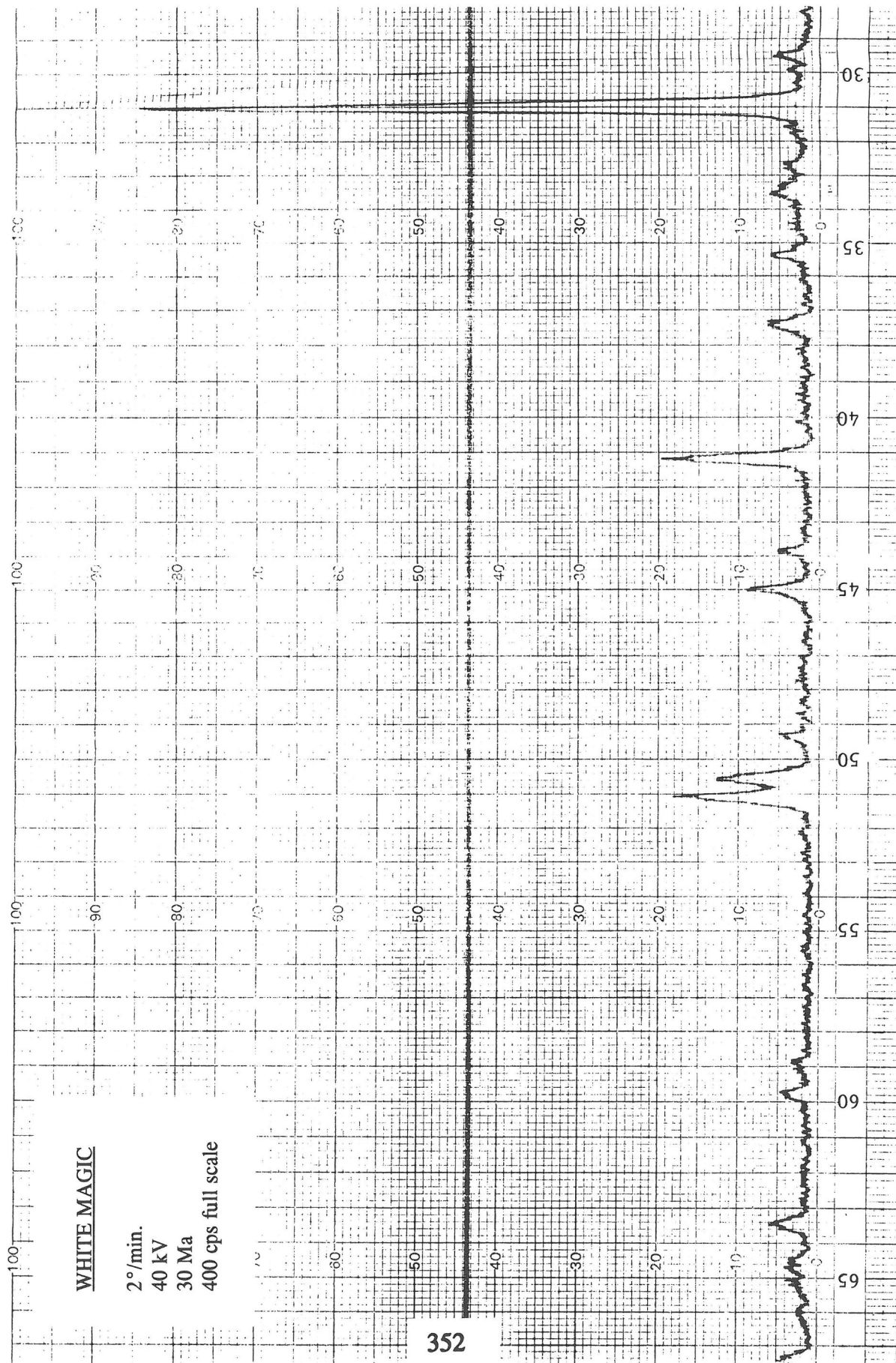
QUESTIONS

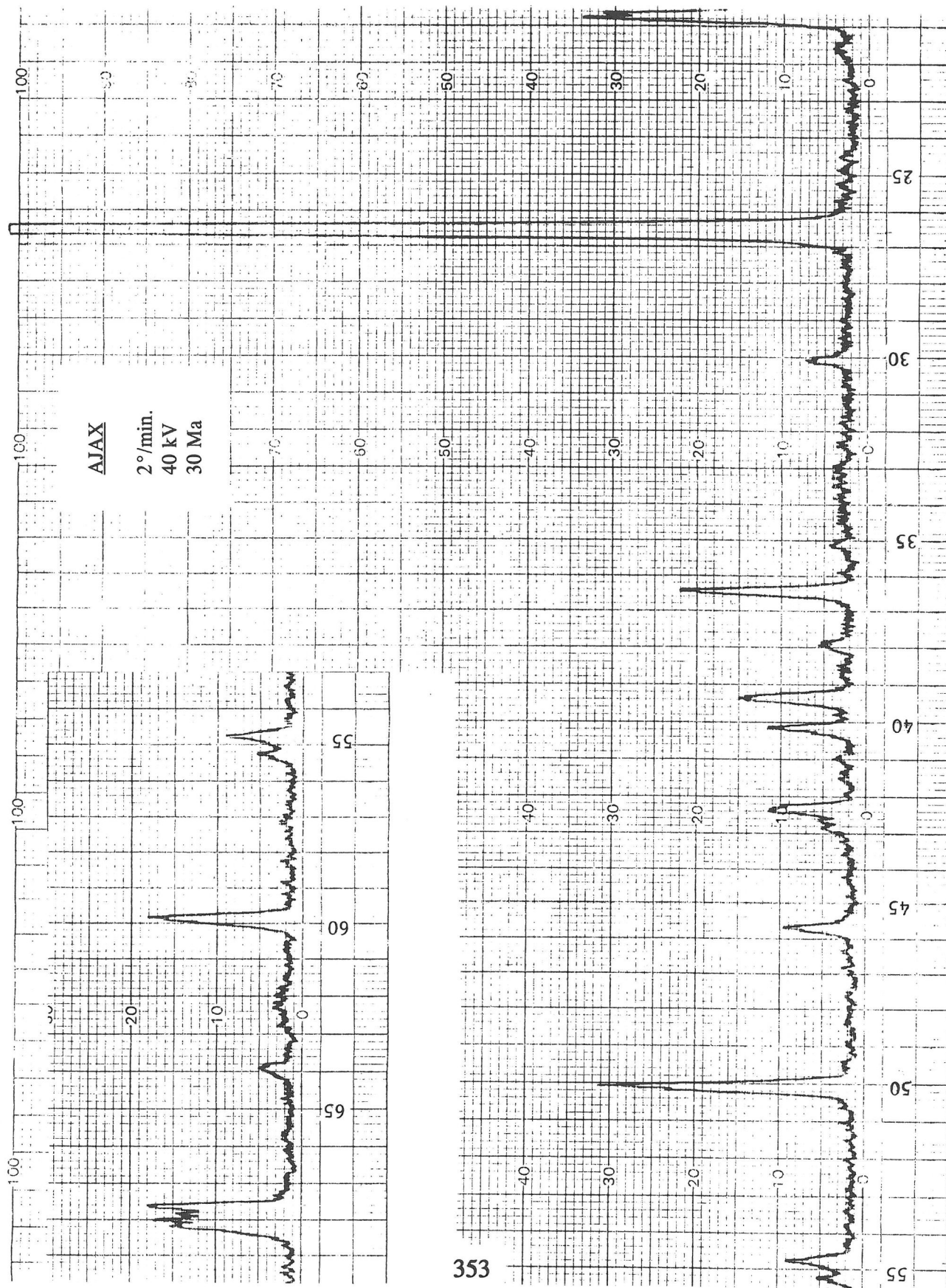
1. List the cleansers in order of **increasing abrasiveness**.
 - 1.
 - 2.
 - 3.
2. Which cleanser will get rid of your bathtub ring most easily?
3. Which cleanser(s) will be the least likely to scratch your bathroom fixtures or your marble sink?
4. What are some possible sources of error between the measured and ideal peak positions?

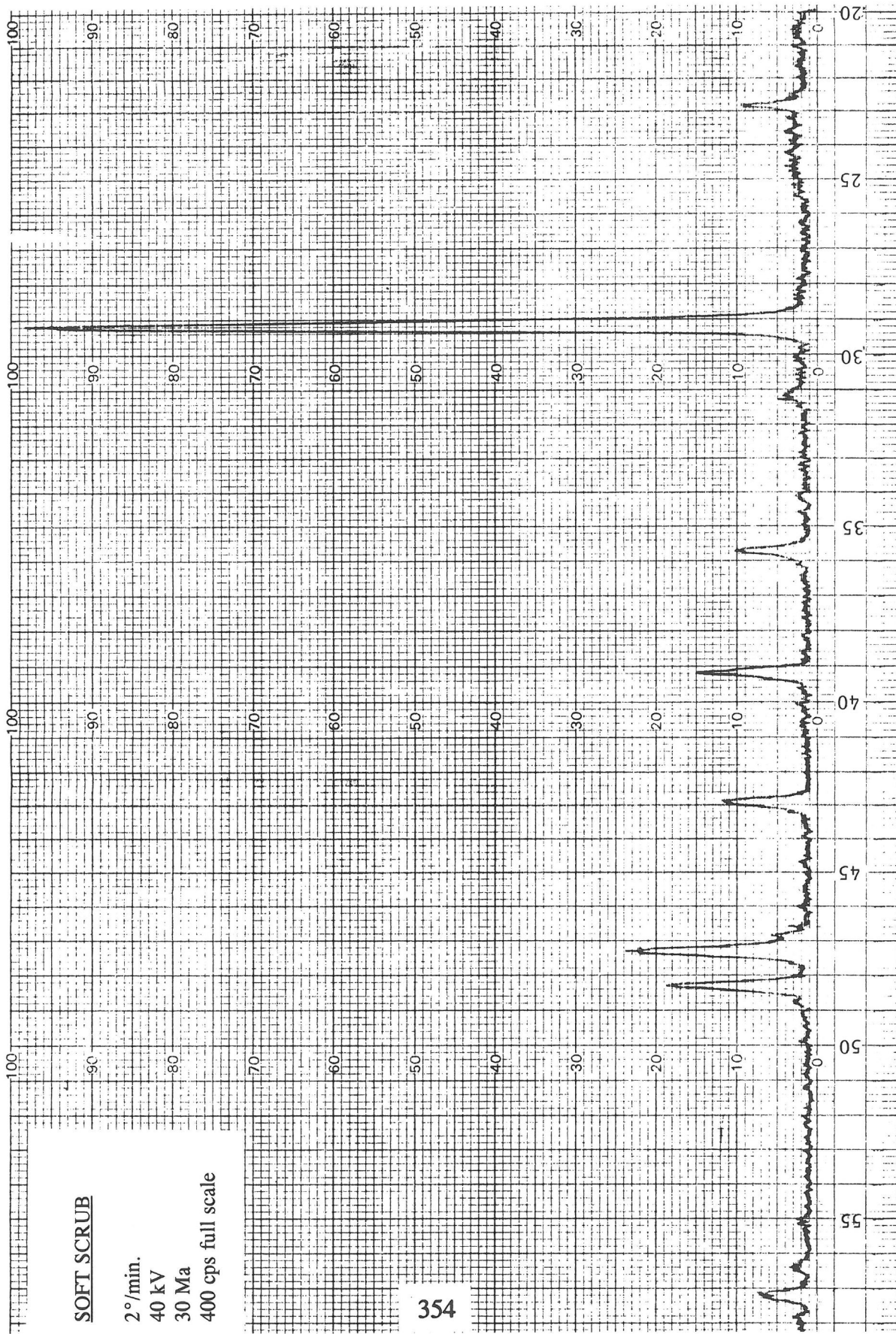
d-VALUES AND HARDNESS OF COMMON MINERALS

The last digit in () refers to the ideal intensity of the peak relative to the intensity of the most intense peak for that mineral. x = 100 (most intense), 9 = 90 %, 8 = 80 %, etc. H = hardness on Moh's hardness scale.

Mineral	H	d-values								
Anhydrite	3.5	3.50(x)	2.85(4)	2.33(2)	2.21(2)	1.87(2)	1.65(1)	1.75(1)	2.09(1)	
Apatite	5.0	2.81(x)	2.78(6)	2.72(6)	3.44(4)	1.84(4)	1.94(3)	2.63(3)	2.26(2)	
Aragonite	3.5	3.40(x)	1.98(7)	3.27(5)	2.70(5)	2.37(4)	2.48(3)	1.88(3)	2.34(3)	
Barite	3.5	3.45(x)	3.10(x)	2.12(8)	2.11(8)	3.32(7)	3.90(5)	2.84(5)	2.73(5)	
Calcite	3.0	3.04(x)	2.29(2)	2.10(2)	1.91(2)	1.88(2)	2.50(1)	3.86(1)	1.60(1)	
Corundum	9.0	2.09(x)	2.55(x)	1.60(8)	3.48(7)	1.37(4)	1.74(4)	2.38(4)	1.40(3)	
Dolomite	3.5	2.89(x)	1.79(3)	2.19(3)	1.78(3)	1.80(2)	2.02(2)	1.39(2)	2.67(1)	
Fluorite	4.0	1.93(x)	3.15(9)	1.65(4)	1.12(2)	1.37(1)	1.25(1)	0.86(1)	1.05(1)	
Gypsum	2.0	7.56(x)	3.06(6)	4.27(5)	2.68(3)	2.87(3)	3.79(2)	1.90(2)	2.08(1)	
Halite	2.5	2.82(x)	1.99(6)	1.63(2)	3.26(1)	1.26(1)	1.15(1)	1.41(1)	0.89(1)	
Muscovite	2.0	10.1(x)	3.36(x)	4.49(9)	2.57(9)	3.66(6)	3.07(5)	2.58(5)	5.04(4)	
Quartz	7.0	3.34(x)	4.26(4)	1.82(2)	1.54(2)	2.46(1)	2.28(1)	1.38(1)	2.13(1)	
Talc	1.0	9.35(x)	1.53(6)	4.59(5)	3.12(4)	2.48(3)	4.56(3)	2.60(2)	2.50(2)	
Topaz	8.0	2.94(x)	3.20(7)	3.69(6)	2.36(5)	2.11(4)	3.04(4)	1.67(3)	2.38(3)	
Wollastonite	5.0	2.97(x)	3.83(8)	3.52(8)	3.31(8)	2.47(6)	2.18(6)	1.83(6)	1.72(6)	







SOFT SCRUB

2°/min.
40 kV
30 Ma
400 cps full scale

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INFORMATION FOR INSTRUCTORS

Purpose

The purpose of this lab is twofold: (1) to demonstrate the ease, utility, and applicability (including uncertainty) of X-ray diffraction (XRD) to mineral identification, and (2) to establish that minerals are a critical, if largely unrecognized, portion of our everyday life.

Previous knowledge required

Typically this lab is to be given as a supplement to a lecture on XRD. This lab assumes that the students have knowledge of the principles and theory behind XRD and other background information that you feel is necessary for an appropriate level of understanding (i.e. when coherent interference occurs and peaks are recorded, etc.).

Lab Materials

XRD patterns have been photocopied for the lab and are part of the lab handout. These patterns were run on an old Phillips diffractometer. Peaks from only one mineral are identifiable in each pattern. Additional materials needed for the lab include a ruler, a calculator and a pencil (I never allow students to use pen in lab).

Introduction to Lab

A short lecture precedes this lab which incorporates:

- sample preparation, random vs. preferred orientation, changes to diffraction patterns caused by various preparation methods, do's and don'ts of sample prep, etc.
- techniques for measuring peaks by hand and expected uncertainty (e.g. measure at 80 % peak height, record the peaks in order of decreasing intensity; 2θ angles can be off by ca. 0.5° leading to calculated d-values being off by ca. 0.02 \AA). Also, remind students of significant figures.
- techniques for searching JCPDS data by hand (e.g. numbers at top of page are for most intense peak but listed in order of second most intense peak, or by computer if you have a CD based catalog).
- permitted difference between measured peaks and those listed (e.g. without internal standards 2θ may be off by 0.5°).
- reasons that the measured peaks may have slightly different d-values from those listed and may have different relative intensities (e.g. machine error, sample height, impurities, compositional variations, order-disorder, grain size, strain**).

**If measured peaks are not corrected using an internal standard or if minerals have compositional variations, etc. that cause the d-values to differ from those listed in the JCPDS files, the students have a difficult time matching d-values to minerals and the lab becomes frustrating. In addition, the relative intensity of the peaks is commonly different than the ideal (especially for lower intensity peaks). Hence, I provide them with the "corrected" d-values, arranged according to the ideal intensity, to aid in identifying the minerals and alleviate frustration.

Options for Customizing the Lab

This lab is extremely versatile and can be easily customized to your laboratory and facilities (or lack thereof) as well as for the time constraints. Below are several methods for presenting the lab, based on equipment and difficulty level.

- Samples:

If XRD equipment and preparation facilities are available, students can prepare their own XRD samples. Then students can run the samples or a technician can run them. If an X-ray diffractometer is unavailable, the attached patterns can be duplicated.

- Peak Identification

Hand or computer methods can be used for peak identification, again, dependent on equipment.

1. Computerized peak search and mineral identification

If the materials have been run on your XRD, peaks will be identified and d-values calculated. These d-values can then be entered into a computerized search routine to identify minerals. Computerized search routines are usually available with the machine software. Other computerized search routines can be used, if a machine is not available.

2. Hand measurement

Students can measure peaks by hand and calculate d-values. For mineral identification, they can match their calculated d-values by one of the following:

- (a) have a JCPDS book (or cards) available for matching d-values.
- (b) photocopy appropriate pages from JCPDS for students to search.
- (c) use selected information from JCPDS (on the back lab sheet) to identify peaks.
- (d) use computerized search routines.

3. Provide students with corrected d-values

Use the d-values provided (in case the peak positions have been displaced and are not corrected). This provides the quickest and least frustrating mineral identification.

- Answers:

Sample 1. White Magic - Dolomite

Sample 2. Ajax - Quartz

Sample 3. Soft Scrub - Calcite

- Other Patterns provided:

An additional XRD pattern is given (Kitty Max: montmorillonite, cristobalite?, illite, kaolinite) as supplemental material at the end of this lab. One copy is blank (for student use) and one has the d-values and mineral ID labelled (for instructor use). This pattern is more challenging which allows you to increase the difficulty of this lab. Minerals were identified with an automatic search routine, (a disclaimer?).

Additional materials and ideas

- These household cleaners are but a few of the household products available for this lab exercise. The supermarket offers any number of other interesting household products for your XRD enjoyment. Reading labels is fun and enlightening.
- As an additional assignment, *have the students bring their own favorite household products to X-ray*. They can peruse the grocery store and cosmetic counters to find any assortment of interesting mineral-containing items. For instance, Crest has TiO_2 but in sufficiently low quantities that we could not see the peaks.
- Additional suggestions (collected from workshop participants) include:
 - Dr. Scholl's products (e.g. kaolin, talc)
 - paint, sunscreens (e.g. rutile or brookite)
 - various cosmetics (e.g. talc, face powder, eye shadow)
 - other cleansers (e.g. Bon Ami with calcite and feldspar, Lava soap with glass)
 - toothpaste (e.g. Crest with sparkles of mica; Tom's of Maine with calcite and fluorite)
 - medicinal products (e.g. Kaopectate with attapulgite, Multivitamins with periclase, calcite)
 - office products (e.g. White Out)
 - food items (e.g. "Chocolate bar" with kaolinite; MacDonald's milkshake (after diluting, washing with detergent, and collecting sludge)-gypsum (or kaolinite?)-two people gave different answers!
- Other "household products" that we ran also contain minerals but have messier/more complicated patterns. Minerals were identified with an automatic search routine. For the more challenging mineral identification:
 - Top Crest Cleanser: quartz, calcite, natrite, dolomite
 - Tidy Cat: illite, montmorillonite, kaolinite, cristobalite?
 - Tums: calcite, natron, talc, but the dominant phase is sucrose!
 - Baking Soda: Nahcolite
 - Sure deodorant: talc, albite (dried overnight in oven); talc (wet)
 - 1996 Ajax: Calcite, dolomite, quartz, natrite (An interesting note, Ajax apparently changed composition in the mid 90's from quartz dominant to calcite. Perhaps it was too abrasive?)

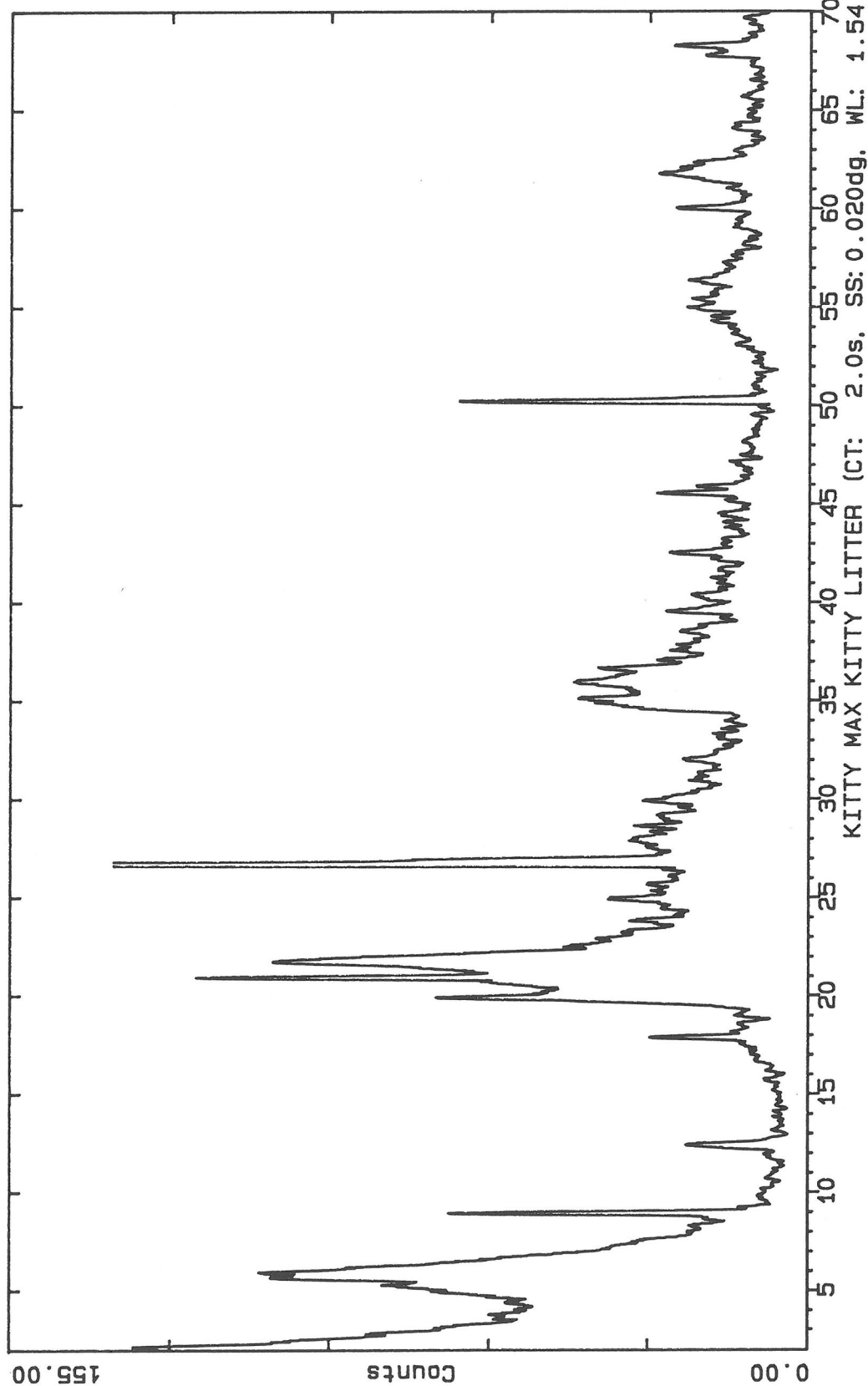
And for more straightforward mineral identification:

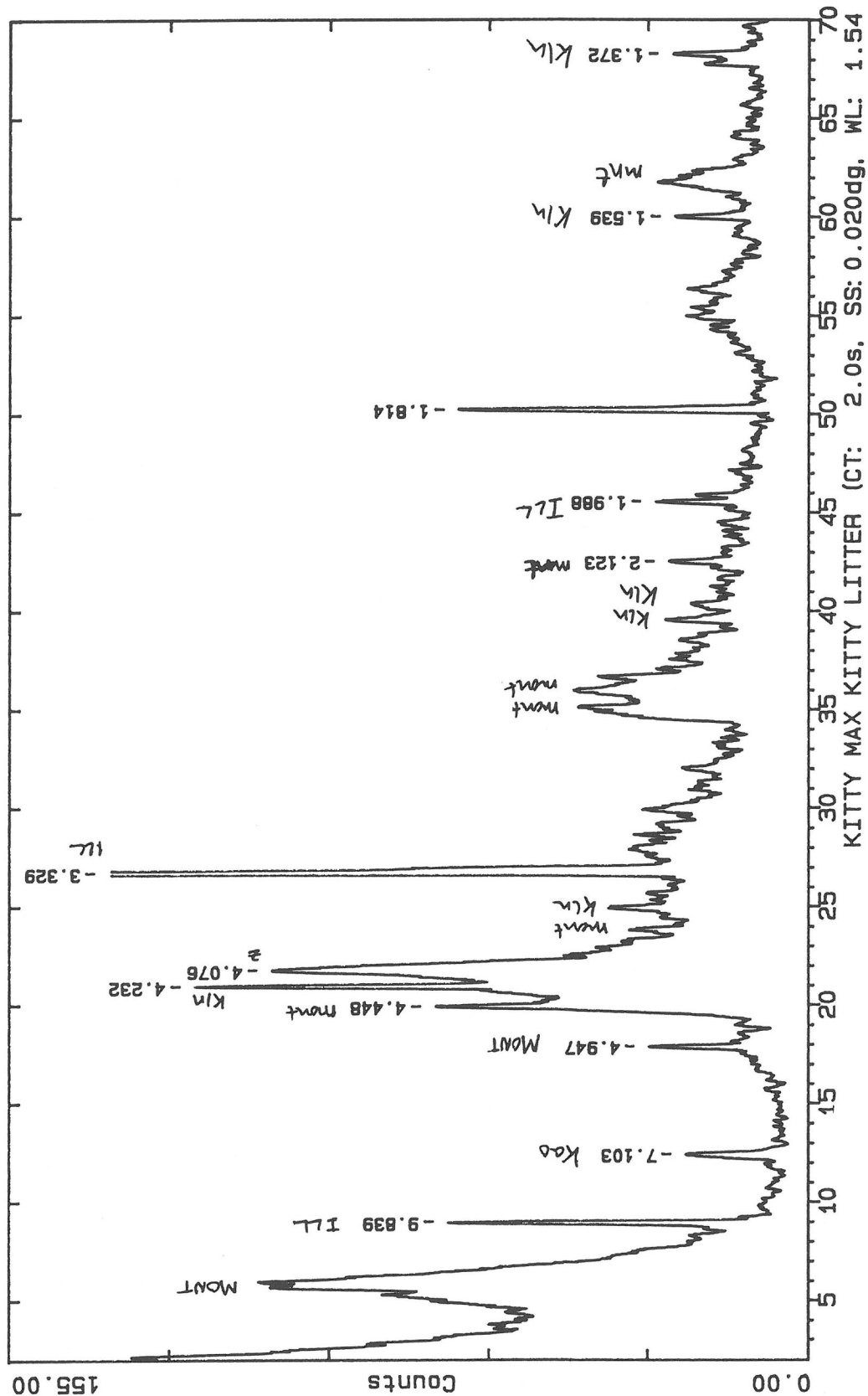
- Table salt and salt substitute

These are very simple, clean patterns. In addition to mineral identification of halite and sylvite, these can also be used to observe the size difference of K and Na (i.e. KCl and NaCl).

2-Theta - Scale

GEOLOGY & GEOPHYSICS DEPARTMENT LSU 17-JUN-1996 13:45





ASBESTOS: MINERALOGY, HEALTH HAZARDS AND PUBLIC POLICY

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BACKGROUND

Asbestos refers to certain minerals that have a fibrous habit and are useful for their insulating, heat and chemically resistant properties. Asbestos has been used extensively for over a century in electrical and heat insulation, fireproofing materials, brake and clutch linings, construction materials, filters and many other applications. Recently, the U.S. has severely restricted the use of asbestos, and has a program for removing asbestos from schools and other public buildings (See Gunter, 1994; Ross, 1995 and references therein). In this laboratory exercise you will have an opportunity to examine the crystal structures, optical properties and health hazards of the common asbestos minerals. The laboratory will reinforce optical microscopic skills that you have learned in mineralogy and show you how mineralogy can be critical to understanding a current public policy issue.

Although mineralogists reserve the designation asbestos for fibrous material with a length:width ratio (aspect ratio) of at least 10:1 (Skinner, et al., 1988), asbestos is defined by OSHA (U.S. Occupational Safety and Health Administration, 1972; Web address is given below) as mineral material composed of any of the six silicate minerals in Table 1 with a length:width ratio of 3:1 or greater, diameter less than 5 μm and length greater than 5 μm .

Table 1. Asbestos Minerals

Mineral	Asbestos name	Mineral Group	Approx. Formula	Comments
Riebeckite	Crocidolite (blue)	clino-amphibole	$\text{Na}_2\text{Fe}^{3+}_2(\text{Fe}^{2+}, \text{Mg})_3\text{Si}_8\text{O}_{22}(\text{OH})_2$	e.g. in pC BIF
Grunerite	Amosite (brown)	clino-amphibole	$(\text{Fe}^{2+})_2(\text{Fe}^{2+}, \text{Mg})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	e.g. in pC BIF, Transvaal, S.A.
Anthophyllite		ortho-amphibole	$\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	Alpine UM rx
Actinolite	Byssolite	clino-amphibole	$\text{Ca}_2(\text{Mg}, \text{Fe}^{2+})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	e.g. East Finland
Tremolite		clino-amphibole	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	rarely asbestiform
Serpentine	Chrysotile (white)	trioctahedral t-o sheet silicate	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	rarely asbestiform serpentinized UM rx, Quebec, Russia, U.S.

ACTIVITY 1 - MINERAL STRUCTURES

The asbestos minerals are either double chain silicates or sheet silicates. We will use the Mineralogy Tutorials CD (Klein, 1995) to review these silicate structures. When you get an opportunity to use the computer, go to *Systematic Mineralogy, Silicates, Inosilicates*.

In *Inosilicates* (chain silicates) look at

- Riebeckite - **photo** is crocidolite, "blue" asbestos
structure - find the tetrahedral double chains, find the strip of M1-M4 octahedral sites between the point-to-point chains, look at the view down the b-axis - note the monoclinic symmetry (all octahedra tilt in the same direction, so **a** is not perpendicular to **c**)
 - Cummingtonite (Grunerite)
photo is grunerite asbestos, which is called amosite or "brown" asbestos
structure - monoclinic, like riebeckite
 - Anthophyllite - **structure** - compare anthophyllite's orthorhombic structure to the monoclinic structure of riebeckite and cummingtonite (two layers of octahedra tilt one way, two layers tilt back the other way; **a** is perpendicular to **c**, therefore, the mineral is orthorhombic)
 - Tremolite (Actinolite)
solid solution shows the variations in chemical compositions of most of the amphiboles you have looked at.
- Go to *Phyllosilicates* (sheet silicates) to look at the serpentine asbestos, chrysotile, and related minerals (Click *index, silicates, phyllosilicates*).
- Chrysotile - **photo** shows cross-fiber chrysotile asbestos
Chrysotile's structure is shown under lizardite, which has the same basic structure.
 - Lizardite - **photo** shows veins of chrysotile (asbestos form) and matrix of lizardite (massive, non-asbestos) serpentine
structure - find the tetrahedral layer (yellow) and the octahedral layer (green) of this tetrahedral-octahedral, t-o, or 1:1 sheet silicate
 - Kaolinite - **structure** - the kaolinite structure is very much like that of lizardite, except that kaolinite is dioctahedral (2/3 of the octahedral positions are filled with trivalent cations, Al^{3+}) while lizardite and chrysotile are trioctahedral (all the octahedral positions are filled with divalent cations, Mg^{2+}). Look at the dioctahedral and trioctahedral illustrations and note the differences in structure of lizardite and kaolinite.
 - Talc - **structure** - talc is a tetrahedral-octahedral-tetrahedral, t-o-t or 2:1 sheet silicate in contrast to chrysotile and lizardite, which are t-o or 1:1 sheet silicates. Note the differences in the pictures of their structures.

But how can a sheet silicate be fibrous?

The octahedral sheet of serpentine filled with Mg^{2+} ($b \sim 9.36 \text{ \AA}$) is slightly larger than the tetrahedral sheet of serpentine filled with Si^{4+} ($b \sim 9.05 \text{ \AA}$). When these two mismatched sheets bond together (share oxygens), they tend to curl with the bigger octahedral sheet outside and the smaller tetrahedral sheet inside. In chrysotile, this results in tightly rolled sheets that form long, thin, flexible fibers. Only under very high magnification in the high resolution transmission electron microscope (HRTEM) can the rolled sheets be seen (Fig. 1).

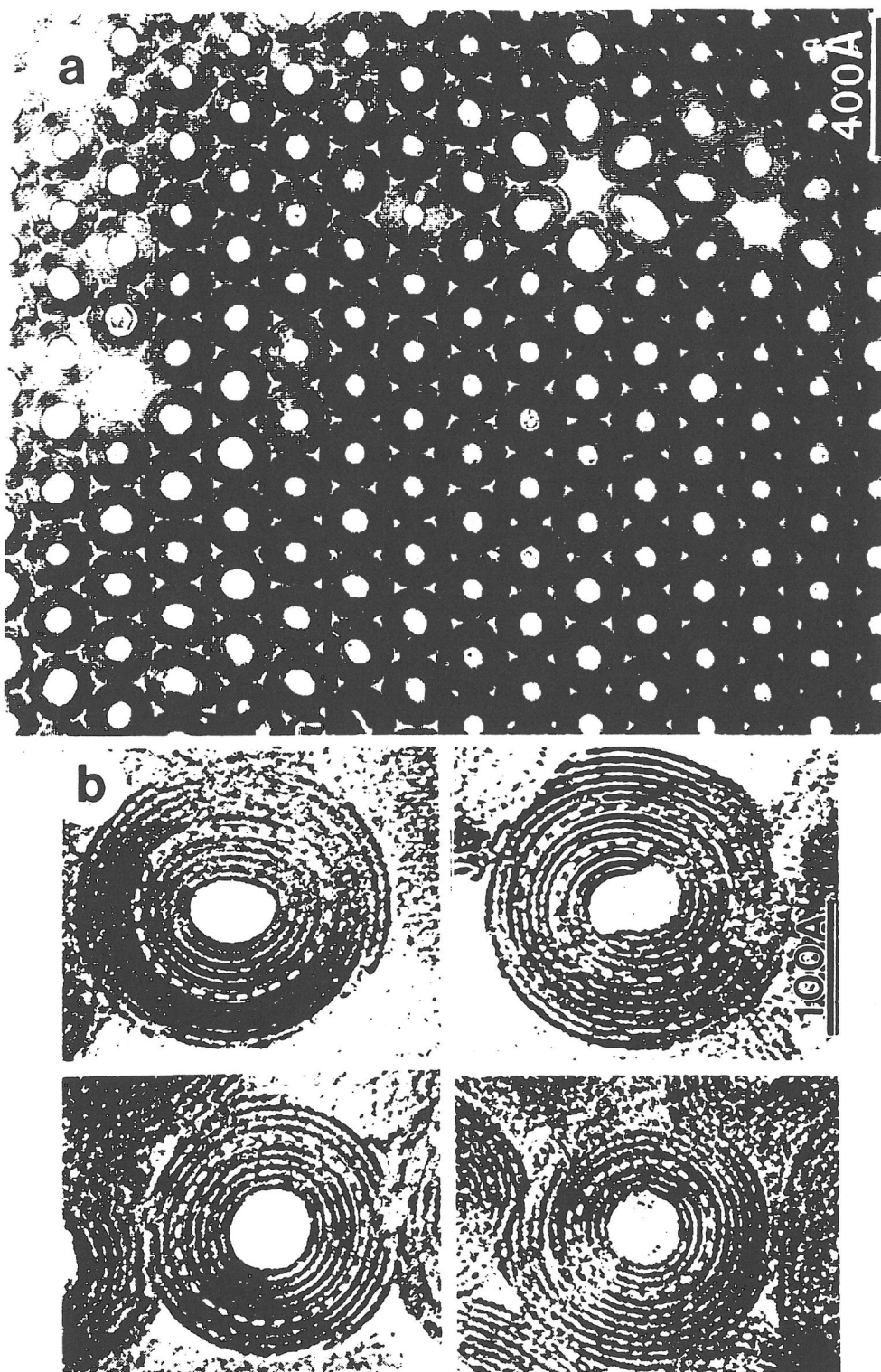


Figure 1. High resolution transmission electron microscope images of chrysotile. a. Packing of chrysotile fibrils in cross-fiber chrysotile asbestos. b. Higher magnification images of chrysotile fibrils with various roll structures viewed parallel to the fibril axis. (after Veblen & Wylie, 1993)

ACTIVITY 2 - MACROSCOPIC AND MICROSCOPIC PROPERTIES

"Hand" samples of each of the types of asbestos are available for you to examine. (Ward's Earth Science, Asbestos Standards Set, 49 E 5840, \$126) The samples are sealed in plastic bags so you won't breathe any fibers. Leave the bags closed and handle the samples as little as possible. Crocidolite ("blue" asbestos) is the most hazardous, and chrysotile ("white" asbestos) poses no hazard to the casual observer. At least one of the samples looks more like cleavage fragments than true asbestos, which one? Write down the properties of each of the mineral samples that you can see with the naked eye, hand lens or binocular microscope. Include approximate length and width of fibers, color, and general appearance.

Optical microscopic properties of asbestos and related minerals are given in Table 2. Your instructor will provide you with grain mounts of three Unknown asbestos minerals labeled Asbestos A, Asbestos B, and Asbestos C (the authors chose amosite, chrysotile and crocidolite) to examine under the petrographic microscope. The refractive index of the mounting medium will be in the standard range of 1.53-1.55. **Record as many of the optical microscopic properties of each sample as you are able to observe. (Your instructor may provide a form on which to record your observations.) If you are not using dispersion staining, give a name to each unknown based on the information in Table 2. Tell which property or properties were most useful for identifying each sample.**

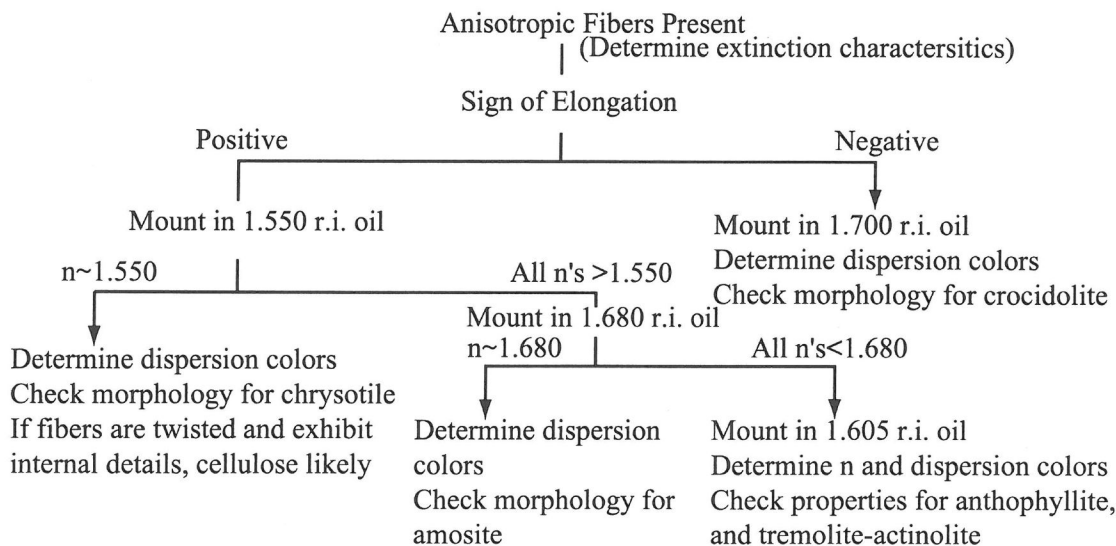
ACTIVITY 3 (OPTIONAL) - DISPERSION STAINING FOR IDENTIFYING ASBESTOS MINERALS

Dispersion staining is an optical identification technique that can be very helpful in identifying and distinguishing asbestos and non-asbestos fibers. The most diagnostic results are obtained when using a "central stop" objective (from McCrone Research Institute, see Information for Instructors) combined with a high-dispersion immersion oil (from Cargille Laboratories). The technique offers several advantages: 1) it is fast and easy and can be used successfully at the undergraduate level; 2) it yields highly diagnostic results that are unambiguous in their interpretation; and 3) it reinforces the concepts of light refraction and dispersion.

Most microscopists think of staining as applying a chemical dye that imparts a characteristic stain, or color, to plant or animal tissue. Dispersion staining is an optical phenomenon in which color is produced, not by a chemical interaction, but by the dispersion of the refractive index of a particle and the mounting liquid (McCrone, 1987). Light dispersion is what produces the colored Becke lines when the refractive indices of a crystal and liquid match. Because the refractive index of an anisotropic crystal will vary with crystal orientation, different dispersion colors will be obtained depending on the vibration direction of light. The dispersion staining technique enhances and clarifies the observed color lines by utilizing a high-dispersion immersion oil coupled with a special objective that blocks-out axial light and produces dark field illumination. For a less-expensive alternative, it is possible (although less satisfactory) to see dispersion colors by using oblique illumination (Bloss, 1961). The relation between crystallographic axes and highly elongated asbestos fibers allows for easy stage manipulation to test staining colors produced parallel and perpendicular to the vibration direction of light. The dispersion staining colors characteristic of each asbestos mineral are listed in Table 2. A flow chart outlining the procedure for identifying asbestos minerals with dispersion staining is shown in Figure 2.

Table 2. Optical Properties of Asbestos and Related Minerals
(from Deer, Howie & Zussman, 1992; McCrone, 1987; diagnostic properties are underlined)

Mineral	Refr. Index (relief)	Birefringence	Extinction	Sign of Elongation	Medium	Dispersion Staining Color n// Color n \perp	Fiber Morphology and Comments
<u>Amphibole Asbestos</u>							
Crocidolite	1.650-1.717 (high)	low	oblique	(-) <u>length fast</u>	1.700	golden-yellow pale yellow	blue, <u>pleochroic</u> , fibrous w/ broom-like ends
Amosite	1.696-1.730 (high)	moderate- high	oblique & parallel	(+) length slow	1.680	golden-yellow blue	<u>straight, stiff, white to tan fibers</u>
Anthophyllite	1.587-1.670 (moderate)	low	<u>parallel</u>	(+)	1.605	yellow	blue, magenta
Actinolite	1.688-1.705 (high)	low- moderate	oblique	(+)	1.605	yellow, pale-yellow	straight or sl. curly, long, acicular fibers
Tremolite	1.599-1.620 (moderate)	moderate	oblique	(+)	1.605	yellow, pale-yellow	straight or sl. curly, thick fibers, star-like
<u>Serpentine Asbestos</u>							
Chrysotile	<u>1.532-1.556</u> (low)	low	<u>parallel</u>	(+)	1.550	magenta	blue <u>long, curly or wavy fibers</u>
<u>Related Minerals</u>							
Brucite	1.560-1.600 (moderate)	low- moderate	parallel	(+) to (-)	1.550	yellow, pale-yellow	fibers, long and straight
Lizardite	1.538-1.560 (low)	low- very low	undulose	(+)	1.550	blue	nonfibrous, platy to blocky
Wollastonite	1.616-1.653 (moderate)	low	parallel & oblique	(+) or (-)	1.625	blue	magenta not very fibrous, short, rod-like



ACTIVITY 4 - ASBESTOS HAZARDS AND REGULATIONS (TURN IN AT YOUR NEXT LAB)

Asbestos has been used extensively for insulation of walls and pipes, as a binder in tiles, as the material of brake linings, for specialized textiles, for fire-proofing and to prevent corrosion on the hulls of ships. Occupational exposure to "blue asbestos" (crocidolite) has been shown to cause mesothelioma, a particularly nasty form of lung cancer, and its use has been banned almost worldwide (not specifically banned in U.S.). Occupational exposure (long-term exposure by mining or manipulating asbestos containing materials (ACM)) to other asbestos minerals is linked with asbestosis and lung cancer, especially in asbestos workers who also smoke. Occupational exposure to chrysotile (serpentine asbestos) is less likely to cause health problems than exposure to amphibole asbestos minerals (Ross, 1995; Mossman, et al., 1990; Skinner, et al., 1988).

Approximately 95% of the asbestos used in the United States is chrysotile. "Non-occupational exposure to chrysotile asbestos, despite its wide dissemination in urban environments throughout the world, has not been shown by epidemiological studies to be a significant health hazard" (Ross, 1984). For comparison, it is estimated that far more children die as a result of lightning strikes, drowning, and high school football accidents, to say nothing of automobile accidents and cigarette smoking, than might die as a result of asbestos exposure in schools. Asbestos removal from public and commercial buildings in the U.S. has cost from \$2 to 4 billion dollars per year in a few recent years. Removing the asbestos temporarily increases the fibers in the air and exposes a new generation of asbestos workers to occupational levels of exposure, and the asbestos containing material (ACM) has to be disposed of safely at great expense.

For your next lab, write a page stating why you believe that the U.S. government should or should not require the removal or repair of asbestos containing material (ACM) from public schools, under what conditions ACM should be removed and whether different asbestos minerals should be treated differently. You may refer to Table 3 and to the reading materials in the lab (see Reference list) to strengthen your arguments. You may also find useful information at these WWW addresses:

<http://www.asbestos-institute.ca/> The Asbestos Institute (a Canadian non-profit institute dedicated to promoting the safe use of asbestos)

http://www.osha-slc.gov/OshStd_data/1910.1001.html U.S. OSHA Asbestos Regulations

<http://www.abwam.com/grossing/refasbes.html> Asbestos Information from a Consulting Firm (Radon Detection Systems)

Table 3. Some Useful Facts about Asbestos and Asbestos Regulations

Asbestos-related Diseases (mainly from Ross, 1995)

Asbestosis- progressive lung fibrosis that causes shortness of breath and eventual death by lung or heart failure. It is caused by all types of asbestos, requires long exposure to high levels of airborne asbestos (occupational), and has a 10-20 year latency period.

Lung Cancer-the same type that is associated with cigarette smoking. It is caused by chrysotile, crocidolite and amosite, especially in those who smoke, requires long exposure to high levels of airborne asbestos (occupational) and has a 10-20 year latency period. There is no evidence of lung cancer from casual exposure to chrysotile.

Mesothelioma-a cancer of the lining of the lung cavity, commonly results in death within 6-18 months of diagnosis. It is caused principally by exposure to crocidolite, to a lesser extent by amosite and has a very long latency period (>20 years). Low, non-occupational exposure to crocidolite can apparently cause mesothelioma.

OSHA definition of asbestos - amosite, crocidolite, anthophyllite, tremolite, actinolite or chrysotile with length:width ratio $\geq 3:1$, length greater than 5 μm and width less than 5 μm

OSHA limit for airborne asbestos in the workplace

(1972) 5 fibers/cm³

(1976) 2 fibers/cm³

(1983) 0.5 fibers/cm³

(1986) 0.2 fibers/cm³

(1992) 0.1 fibers/cm³

Mean concentration of asbestos fibers in air from 219 schools with asbestos containing material (ACM) in the U.S. and Canada

0.00022 fibers/cm³ (Ross, 1995, from Health Effects Institute-Asbestos Report, 1991)

Mean concentration of asbestos fibers in outdoor air

0.00039 fibers/cm³ (Mossman, et al., 1990)

Asbestos abatement contractors are released from liability after cleanup (EPA-AHERA (Asbestos Hazard Emergency Response Act, 1986)) if airborne asbestos in the school is less than 0.005 fibers/cm³

Number of schools in the U.S. estimated to have ACM

31,000 (Wilson, et al., 1994)

Comparative Risks (expressed two ways)

(from Mossman, et al., 1990)	
Cause	Annual Rate (deaths per million)
Long-term smoking	1200
Home accidents (ages 1 to 14)	60
Motor vehicle accident, pedestrian (ages 5 to 14)	32
Drowning (ages 5 to 14)	27
High school football (1970 to 1980)	10
Aircraft accidents (1979)	6
Whooping cough vaccination (1970 to 1980)	1 to 6
Asbestos exposure in schools	0.005 to 0.093
(from Ross, 1995)	
Nature of Risk	Risk of Death (per one million lifetimes)
Smoking (all causes)	210,000
Motor vehicle accidents	17,000
Home accidents	8,400
Falls	5,600
Drowning	2,100
Frequent airline passenger	1,000
Living in a brick building (radiation)	350
Electrocution	350
Tornadoes	49
Lightning	35
Hurricanes and tropical cyclones	28
Exposure to asbestos in schools (6 hr/d, 5 d/wk, for 14 yrs at 0.00022 fibers/cm ³)	1

ACKNOWLEDGMENTS

We thank John Brady and other members of the Organizing Committee for organizing the Teaching Mineralogy Workshop and the Workshop participants who took the role of students in this laboratory for their suggestions and lively discussion. LeeAnn Srogi, David Walker and Dexter Perkins are thanked for trying this laboratory in undergraduate classes and providing very helpful reviews.

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INFORMATION FOR INSTRUCTORS

Students in any particular mineralogy class will not necessarily know how to test all of the optical properties referred to in this laboratory exercise. Feel free to adapt the lab and encourage the students to apply any techniques they know how to use.

Source of Materials

Asbestos samples were purchased from Ward's Earth Science (Asbestos Standards Set, 49 E 5840, \$126 (includes Clinochrysotile, Thetford, Quebec; Chrysotile, Globe, Arizona; Actinolite, Chester, Vermont (cleavage fragments); Anthophyllite, Udiapur, India; Crocidolite, South Africa; Tremolite, Harquahala Mts., Arizona; Amosite, South Africa)). Grain mounts were made by H.L. from the samples described above (careful handling in a hood with paper face mask). The CD-ROM, Mineralogy Tutorials (ISBN 0-471-10996-7; current price \$395) was purchased from John Wiley & Sons. The central-stop objective (part # 289F; cost approximately \$500) and information about the dispersion staining technique were obtained by S.H. from McCrone Research Institute, 2820 S. Michigan Avenue, Chicago, Illinois 60616-3292, phone 800-622-8122 (URL <http://www.mccrone.com>). High-dispersion oils (approximately \$60 per bottle) can be obtained from R.J. Cargille Laboratories Inc., phone 201-239-6633.

Handling Asbestos

Hand specimens for this laboratory are sealed in zip-lock plastic bags (double bagging for crocidolite and amosite). Grain mounts are permanently sealed in CR-1 Cover Glass Mounting Medium (Wards 37 E 9550) with a refractive index of 1.535. Direct handling (e.g., preparation of microscope mounts) of amphibole asbestos and bulk samples that may contain crocidolite or amosite asbestos should probably be done in a hood. Limited handling of chrysotile is not believed by most mineralogists to be hazardous to students or instructors.

INTRODUCTION TO THE PROPERTIES OF CLAY MINERALS

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Required materials: montmorillonite, balance, 7 beakers (150 ml), saturated solutions of NaCl, MgCl₂, and CaCl₂, squeeze bottle with pure water, ring stand, 1" glass (or Plexiglass) tube, stirrer, rubber stopper with hole for glass tube, 1 large beaker (800 ml), cotton balls, tweezers, quartz sand, funnel, watch with second hand, methylene blue

INTRODUCTION

"Clay refers to naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when fired or dried." The minerals found in clay are generally silicates less than 2 microns (one millionth of a meter) in size, about the same size as a virus. Clays are very abundant at the earth's surface; they form rocks known as shales and are a major component in nearly all sedimentary rocks. The small size of the particles and their unique crystal structures give clay materials special properties, including cation exchange capabilities, plastic behavior when wet, catalytic abilities, swelling behavior, and low permeabilities.

Clay minerals are used as coatings on paper to produce whiteness and to allow the proper absorption of ink, to extend the life of rubber in tires, in concrete, as catalysts in many industries, to purify oils, in pharmaceuticals, in the ceramic industry to make bricks, chinaware and porcelains, and in many other industries and processes. Clay minerals, and specifically montmorillonite, are used as clay barriers for nuclear and chemical wastes because of their cation-exchange capabilities, low permeability, and long term structural stability.

To understand cation exchange capability, it is necessary to learn a little about the crystal structure of clay minerals in general and montmorillonite specifically. Cation exchange affects the mechanical and physical properties of the clay. The purpose of this laboratory is to illustrate the importance of chemistry on the physical properties of montmorillonite, the clay mineral most often used to isolate dangerous waste materials from the environment.

STRUCTURAL ASPECTS

Clay minerals are commonly phyllosilicates or layer silicates. These minerals have platy morphology because of the arrangement of atoms in the structure. There are two basic components to the structure: a sheet of corner-linked tetrahedra and a sheet of edge-sharing octahedra. Figure 1 illustrates the linkage of atoms to form both tetrahedra and octahedra, whereas Figure 2 illustrates the linkages of each to form the two varieties of sheets.

Tetrahedral sheets. The dominant atom in the tetrahedron is the Si^{4+} cation, but the Al^{3+} cation can occur also at this site. This is an important point, because the substitution of Al^{3+} for Si^{4+} produces a charge deficiency that must be balanced somewhere else in the structure. We will return to the concept of charge deficiency below, although in a somewhat different sense involving octahedra.

Note in Figure 2 that the tetrahedra link up to form a sheet by the sharing of three corners of each tetrahedron. For each corner that is shared between two tetrahedra, only one oxygen is involved in the linkage. Compare this to the two oxygens involved in two individual tetrahedra. Thus, it takes fewer oxygens to complete a sheet of tetrahedra compared to the same number of individual and unlinked tetrahedra. If we add the number of oxygens around each tetrahedron by "dividing" up an oxygen linking two tetrahedra (so each tetrahedron then has one-half an oxygen), then there are two and a half oxygens per tetrahedron (or 10 oxygens per 4 silicon atoms). Because the O atom has a 2- charge, then a tetrahedral sheet with Si_4O_{10} composition will have an overall charge residual of 4- ($4 \times 4^+ = 16^+$ vs $10 \times 2^- = 20^-$). Because the overall structure must be charge neutral, another part of the structure, the octahedral sheet, must compensate or compensate in part for this charge residual.

Octahedral sheets. The octahedral sheet is composed of edge-sharing octahedra. Different phyllosilicates have different cations in the octahedra. For phyllosilicates with relatively high-charged, trivalent cations (e.g., Al^{3+}) in the octahedra, it is required that for every two octahedra that contain Al^{3+} , there is an empty octahedron. The pattern of Al^{3+} and vacant sites is illustrated in Figure 3, and is referred to as a "dioctahedral" sheet. Alternatively, a "trioctahedral" sheet forms where all three sites are occupied, which occurs for octahedra occupied by divalent cations (e.g., Mg^{2+}). Many phyllosilicates contain a small number of divalent cations in a dioctahedral sheet (e.g., Mg^{2+} substituting in small amounts for Al^{3+}) or, conversely, a small number of trivalent cations in a trioctahedral sheet (e.g., Al^{3+} substituting in small amounts for Mg^{2+}). Where this happens, a small deficiency in charge occurs that must be compensated elsewhere in the structure. As noted above, similar charge deficiencies can develop in the tetrahedral sheet as well.

Nearly all phyllosilicates have hydroxyl (OH^-) ions involved in the linkages to form sheets, in addition to the oxygens. A hydroxyl ion is an oxygen atom with a hydrogen attached. The overall charge of a hydroxyl ion is 1- because the hydrogen atom has a 1+ charge and the oxygen has a 2- charge.

Layers. The tetrahedral and octahedral sheets may be considered modular components of a phyllosilicate. It is now necessary to join the two sheets. The lateral dimensions of the two sheets are approximately equal so it is possible to join them together. As we found with the tetrahedral linkages to form the tetrahedral sheet, it takes fewer oxygens to complete the linkage than if we had two individual sheets, because there is a common junction between the two. This common junction is a plane of oxygen and hydroxyls that belongs to both the tetrahedral sheet and the octahedral sheet (Figure 4). For the case of montmorillonite, there are two tetrahedral sheets, inverted relative to each other, and with an octahedral sheet sandwiched between. Thus, some of the oxygens that belong to the tetrahedral sheets also belong to the octahedral sheet. Only the hydroxyl ions do not link directly to the tetrahedra.

REPRESENTING COORDINATION POLYHEDRA

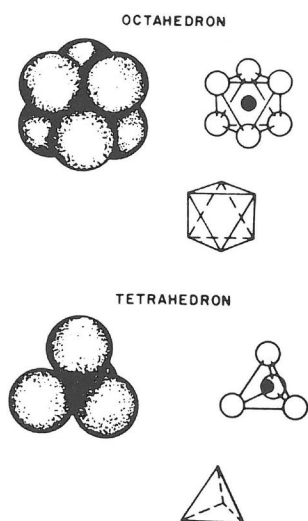


Figure 1. Examples illustrating several ways to represent coordination octahedra and tetrahedra. The large spheres are usually oxygen atoms enclosing a "site" where smaller cations may reside. (Figure courtesy of K. Rodolfo)

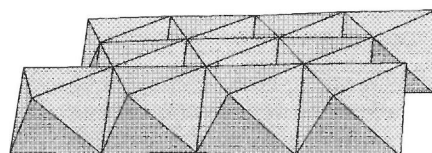
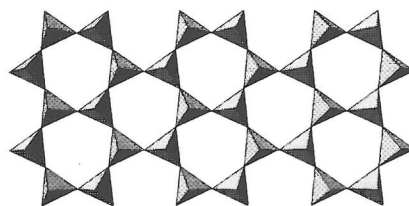


Figure 2. Tetrahedra may be linked through a corner oxygen to form a tetrahedral sheet and octahedra may be linked by edge sharing to form an octahedral sheet. (The two sheets have different scales.)

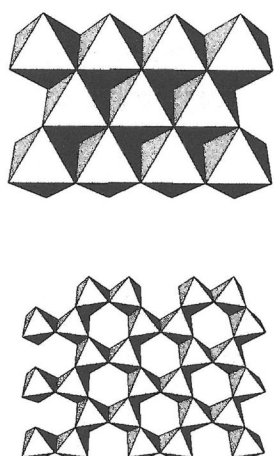


Figure 3. Octahedral sheets occur as either trioctahedral (top) or dioctahedral (bottom), depending on whether a vacant site occurs or not. (The two sheets have different scales.)

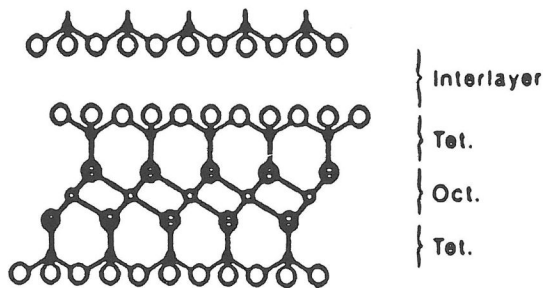


Figure 4. A layer is illustrated in side view. The octahedral sheet is sandwiched between two opposing tetrahedral sheets. (after Koster van Groos and Guggenheim, 1990)

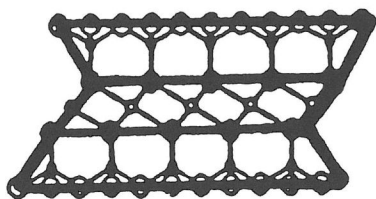


Figure 5. Illustration simplifying the sheets for easy drawing. Note the modular components as indicated by the dark lines.

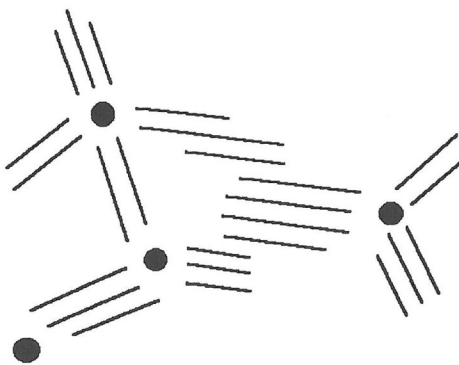


Figure 6. Schematic showing how Cl^- ions (solid circles) can cause flocculation by adhering to broken (external) edges of clay particles.

Although the tetrahedral and octahedral sheets extend laterally over many hundreds of Angstroms (an Angstrom is 10^{-8} cm), we can simplify the drawing of the layers by using finite widths, as in Figure 4. In turn, we can simplify these representations even further by drawing modular units that represent tetrahedra and octahedra (Figure 5) and by leaving out the circles and lines that represent the atoms and bonds (not illustrated). As long as we understand and agree to this drawing as a representation of the structure, then we can use these diagrams as a convenience.

Charge balance and the layer. Assuming for simplicity that we do not have any substitutions in an aluminous dioctahedral layer when the tetrahedral cations, octahedral cations, oxygens, and hydroxyl groups are all taken into account, the resulting chemical composition of the layer is $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$. If we examine the charges for this layer we find that there is complete charge balance (e.g., for positive charges: $2 \times 3^+ + 4 \times 4^+ = 22^+$ vs for negative charges: $10 \times 2^- + 2 \times 1^- = 22^-$). A phyllosilicate of this composition is known in nature and is called pyrophyllite.

The composition of the layer in montmorillonite, however, is less ideal, with chemical substitutions of a small amount of Mg for Al in the octahedral sites. Thus, the layer has a composition close to $(\text{Mg}_{0.4}\text{Al}_{1.6})\text{Si}_4\text{O}_{10}(\text{OH})_2$, where 0.4 Mg has substituted for some Al in the octahedral sites (compare the layer chemistry to that in the preceding paragraph). If we examine the charges in this layer, we find that there are 0.4 more negative charges than positive charges (e.g., $0.4 \times 2^- + 1.6 \times 3^+ + 4 \times 4^+ = 21.6^+$ for positive charges vs $10 \times 2^- + 2 \times 1^- = 22^-$ for negative charges). This may not seem like much to you, but it makes a world of difference in the behavior of montmorillonite compared to other phyllosilicates. All crystal structures must be charge neutral. Thus, the net negative charge of 0.4 on the layer must be compensated, and montmorillonite does this by having positively-charged material (and H_2O) between the layers. This region is called the "interlayer" space (Figure 4).

Interlayer material. It does not really matter what is in the interlayer, as long as it is positively charged and atomic or molecular in size. Thus, it is possible to place cations such as Na^{1+} , K^{1+} , Ca^{2+} , or Mg^{2+} in the interlayer, or even organic molecules. Often, depending on the nature of the cation, polar H_2O molecules enter the interlayer. For example, copious amounts of

H₂O go into the interlayer with Na, whereas many fewer H₂O molecules enter the interlayer with Ca. Overall charge balance is always maintained, however, because H₂O is neutral. Also, charge balance is maintained with the number of cations entering the interlayer space, as in the case where half as many Ca cations enter the interlayer than Na, because the charge on Ca is twice that of Na. In addition, it is fairly easy to replace interlayer cations with other material, as long as there is a large amount of that material in the immediate environment. For example, an aqueous (water) solution containing many Na cations around a montmorillonite grain will readily allow for Na to exchange for K, if K is in the interlayer. Therefore, these cations are often called "exchangeable cations". The fact that exchangeable organic molecules can enter into the interlayer explains why montmorillonite is useful to purify oils, since oil contaminants with a positive charge will enter the interlayer. However, non-polar and neutral oil contaminants may not enter the interlayer very readily.

To understand how cation exchange works, it is necessary to define "internal" vs "external" surfaces of a clay particle and to determine how they attract cations and anions. The internal surfaces are the two planes of atoms on either side of the interlayer space at the base of the tetrahedral sheet. External surfaces are the broken edges of the layer. Because there are no broken bonds on the internal surfaces and the negative charge on the layer originates well within the layer (at the octahedral sheet), the internal surfaces attract cations and other positively charged particles. In contrast, however, the external surfaces generally attract negatively charged anions because the cations (e.g., Si⁴⁺, Al³⁺) closest to the broken surface within the clay require the negative charge to compensate.

Cation exchange is most readily achieved by dissolving a salt in water so that the cation dissociates from the anion. Thus, for example, NaCl will dissociate to form Na¹⁺ and Cl¹⁻ ions in water. The Na¹⁺ is then available to enter the interlayer to replace whatever cation happens to be present, provided that the concentration of Na in solution is sufficiently high. Natural montmorillonite generally contains a mix of cations, including Na, Ca, K, Mg, Al, etc. End-member compositions (e.g., pure Na-exchanged montmorillonite or pure K-exchanged montmorillonite) have specific and unique properties, so it is useful to make different end-member composition by cation exchange.

If only Na¹⁺ is present in solution, then the individual clay particles would float freely in the water, which is called "dispersion". However, the negative anions (Cl¹⁻) in solution attach to the external surfaces of the clay layers and cause "flocculation" or the clumping of particles (Figure 6). As the clay flocculates, it falls to the bottom of the glass or beaker.

A cation exchanged clay in a salt solution can be made to disperse by washing in pure water and removing the Cl ions (to be replaced by polar H₂O molecules), since the Cl ions are only weakly bonded to the edges. Because the Na is relatively tightly bound within the interlayer, washing the clay will not affect the Na cations. Usually, it takes several washings (sometimes up to six) to remove fully the Cl. Na-exchanged montmorillonite generally requires fewer washings than other cation exchanged montmorillonites to achieve dispersion. Depending on what experiments or processes are planned, sometimes it is more convenient to work with either a dispersed or a flocculated clay.

EXPERIMENTAL PROCEDURES

Part I.

The purpose of this part of the laboratory is to illustrate the cation exchange capabilities of montmorillonite and the effect of cation exchange on the physical properties of the clay. We will cation exchange Na^+ , Mg^{2+} , and Ca^{2+} into the interlayer of the clay.

1. Weigh 2 g. of montmorillonite and place it into a 150 ml. beaker.
2. A "saturated" solution is one in which no additional solid can be dissolved in water. Your instructor has prepared a saturated solution of NaCl. Decant (pour off just the fluid portion, making certain that no solid is poured also) approximately 30 ml. of saturated NaCl solution into the beaker with the clay (label the beaker: Clay + Na). Stir briefly for 10-15 seconds and then set aside.

Repeat the same procedure for clay + MgCl_2 solution and clay + CaCl_2 solution.

3. Allow each beaker to stand until most of the clay settles to the beaker bottom (about 5 minutes). The fluid may remain murky. The high chloride (Cl) content of the fluid prevents dispersion. Let's now remove the Cl ions by washing with water.
 - a. Decant the fluid from the clay--be very careful not to lose too much clay.
 - b. Add water to the clay residual so that it is at the 60 ml. level on the beaker and stir. Again, allow the clay to settle for about 5 minutes. Are there any differences between the way the Na-montmorillonite appears compared to the other two?

- c. Decant each beaker for a second time. Again, be careful not to lose the bulk of the clay in each beaker. (It may be necessary to decant fluid, allow to settle for a bit longer, and then to decant again.) No add another 60 ml of water. Stir and allow to settle for about 5 minutes. Re-examine the clay water mixes and discuss the differences.

4. Decant as much fluid from each clay/water mix as possible, being careful not to lose the clay.

Set the beakers containing the wet clay aside for Part II.

Part II.

The purpose of this part of the laboratory is to examine the effect on permeability of different compositions of montmorillonite clay. We will examine the flow of water and salt water through a column of (a) sand and (b) montmorillonite + sand mix.

1. Place three or four cotton balls at one end of the glass column and use a rubber stopper with a hole to seal that end. Place the small glass tube in the stopper, so that water will be able to flow from the stoppered end without forming a reservoir. This is the bottom end. Leave the top end open. The purpose of the cotton is to allow the fluid to drip from the hole without the loss of clay or sand.
2. Place sand (enough to fill the glass column half way) in the large beaker and add water until the sand is wet. Pour off any excess water. Using the funnel, fill the column from the top end with the wet sand. It helps to tilt the column, so that the sand works its way down the side of the glass column. Use the squeeze bottle to wash the sand down the glass, but use water sparingly so that the sand does not stratify (form layers of equal size sand grains). Avoid having large (air) voids in the sand column. Fill the column only halfway. Mount the column on a ring stand, with a beaker at the column base to catch water. Allow any excess water to drip out of the column and, once the dripping stops, empty the beaker.
3. Add 50 ml. water to the column and time how long it takes to pass through the column (i.e., how long it takes to recover about 50 ml. in the beaker at the column base). The actual amount of water that is collected will vary depending on how wet the initial sand was. However, the collected amount will be approximately 50 ml. and the flow will be essentially complete.
time = _____
4. Repeat step 3 with 50 ml of saturated NaCl solution (NOT the clay-water mix).
time = _____
5. Remove the sand from the column and place it in the large beaker. Add water to the sand, stir, and then decant. Wash the sand in this way several times to remove the NaCl. Try to eliminate any excess water.
6. Decant the residual water from the Ca-exchanged montmorillonite from Part I. Add one-half of the amount of clay to the wet sand and stir in well. It is best to try to stir and fold the clay and sand mix by hand. It is important that you make a sincere effort to stir in the clay uniformly throughout the sand.
7. Place the clay/sand mix into the column. As before, place a cotton ball at the bottom first. Also, it is permissible to add a small amount of water to aid in getting the mix to flow into the funnel, but use water sparingly. It may be necessary to decant any excess water off the top of the column. (Do NOT allow the clay in the excess water to settle on the top of the column. Therefore, decant this excess water off.)
8. Add 50 ml. pure water in to the column top and determine the amount of time it takes to collect in the beaker at the bottom. time = _____
9. Repeat the experiment by timing 50 ml. of NaCl saturated fluid. time = _____
10. Now add 50 ml. of water to the top of the column and record the time it takes to drain. time = _____
Empty the beaker. Repeat with 50 ml. more water. Again time the results. time = _____
Empty the beaker before continuing. Finally, repeat a third time. time = _____

11. Add a small amount of methylene blue dye to 50 ml. of water. Add this solution to the top of the column and determine the amount of time it takes to collect 50 ml. in the beaker at the column base. What do you find?

If time permits:

Each group of students should report the times for 50 ml. flow of saturated NaCl solution through the sand column, and times for saturated NaCl solution and three times for pure water in the sand + clay column. Discuss the possible reasons for the variations in times between each set of measurements.

Discussion after completing the experiments:

1. What was the purpose of adding water to the column in Part II, Question 10? Remember, we used Ca-exchanged montmorillonite in the experiment and added NaCl-saturated water to the column first.
2. Na-exchanged montmorillonite is found naturally and in large quantities in bentonites. Bentonites are extensive beds derived from volcanic ash (natural glass) deposits that have recrystallized as montmorillonite. This material is used in many industrial processes and for clay liners in chemical and radioactive waste disposal sites
 - a. How effective would the clay liner be if the ground water contained appreciable NaCl?
...only pure (fresh) water?
 - b. What would you have to know about the nature of the chemicals in a chemical waste dump, if montmorillonite is to be used as a clay liner. What would the effect of different chlorides have on the effectiveness of the liner?

LOW LEVEL RADIOACTIVE WASTE DISPOSAL: DISCUSSION

Background. The Lilly Light Company was active from 1946 to 1952 in making luminescent light dials from thorium in West End Chicago, a town of about 20,000 in 1946. During this period, the company employed about 300 women, who painted numbers on the watch dials with radioactive paint. It should be remembered that this period was before the time when radioactivity was considered potentially harmful. In fact, X-ray machines were commonly used in shoe stores to determine if the shoe-size was correct by simultaneously X-raying the foot in the shoe, and radiation therapy was a common treatment for acne.

The Lilly Light Company maintained over 100 buildings in West End Chicago. Almost all were contaminated by thorium and related mine tailings. The contamination consisted generally of particles of thorium dispersed throughout large volumes of construction material. Thorium (^{230}Th) has a half life of 80,000 years, and the general "rule" for more common radioactive waste is that disposal sites should be constructed to maintain radioactive materials for about 10 half lives. Although radioactivity from low level waste should be obviously avoided, an equally important problem is where radioactive particles become airborne as dust. Once inhaled, such particles remain trapped in the lungs to damage tissue over long periods.

In 1952 the Lilly Light Company filed for bankruptcy and was purchased by the Nosean Mining Company, as part of a larger take-over of several companies. The Chairman of the Board of Nosean considered briefly the manufacture of Nosean "Nite-glo Facial Tissues", by combining the concept of thorium-based luminescence with softness and strength, to produce a tissue that will glow in the dark on every night table in the U.S. This scheme failed to gain momentum, and Nosean concentrated its efforts elsewhere, although the company remained in control of the assets of the Lilly Light Company.

Over the years since the bankruptcy of Lilly Light, the town (now city) developed around the abandoned buildings. The buildings, which covered many city blocks, were protected by an aging chain-linked fence. The fence was routinely breached by children. The community was becoming concerned that the property had become an "attractive nuisance" for the neighborhood children and, furthermore, it was concerned about the rapidly deteriorating buildings, several of which already had collapsed roofs. In addition, the land had become an "eyesore", and property values around the area were depressed.

In 1978, the State of Illinois petitioned the U.S. Nuclear Regulatory Commission (NRC) to decommission the site. Because thorium production and use was involved, the NRC had jurisdiction over the site. Although the Nosean Mining Company did not gain greatly from its purchase of Lilly Light and had no involvement in the use of thorium on the site, it had legal responsibility as property owner of the land. The City of West End Chicago was involved in the litigation as an "interested party".

The NRC ordered Nosean Mining to examine the site and to suggest remediation. It was generally understood that the site would be decommissioned--Nosean did not want a long-term commitment for maintaining the site, the NRC had an ever-burgeoning number of sites in the U.S. and did not want long-term jurisdiction if an alternate approach could be found, and the City and State wanted to remove the blight so property values would rise.

Site conditions. Nosean found that the vast number of buildings were contaminated with thorium dust and particles. Contamination included building materials (wood beams, brick, etc.), soil around the buildings, and soil and clay from retention ponds apparently used in the processing and concentration of ore. By 1981, Nosean workers were ordered to wear protective suits to avoid contamination, and the old fences were replaced with newer chain-linked fences. Warning signs were placed around the site. There was concern that as contaminated buildings collapsed and deteriorated further, more thorium particles would be exposed to wind and rain, thereby spreading to areas away from the site. There was some evidence that this had already happened. However, thorium migration downwards to the water table under the former retention ponds was very minimal because thorium oxides are not very soluble.

Remediation. Nosean picked a plan to dispose of the low level radioactive waste at the Lilly Light plant site. It was argued that, although sites may be available downstate, transport of the large volumes of waste would create greater danger than disposal at the plant site. For example, according to Nosean Mining, unacceptable amounts of dust would be created at the site by loading onto trains and trucks, further dust would be made airborne during shipping and unloading, and the containment of water used for dust abatement would be difficult to handle. It would also cost the company nearly \$60 million for transportation and more to acquire land downstate. Some estimates were as high as \$87 million. On-site disposal, on the other hand, would only cost an estimated \$20 million.

Nosean Mining extensively described the characteristics of the site at West End Chicago. It is underlain by glacial till, including kaolinite, sands and gravel. The water table is not near the surface. The containment cell was first described as illustrated in Figure 1. It consists of a large clay cover and "manufactured" clay lining of locally derived clay. Because the site will be decommissioned after it is assured that the cell has "stabilized", Nosean Mining suggested that the City would be able to use the top surface as clay-based tennis courts.

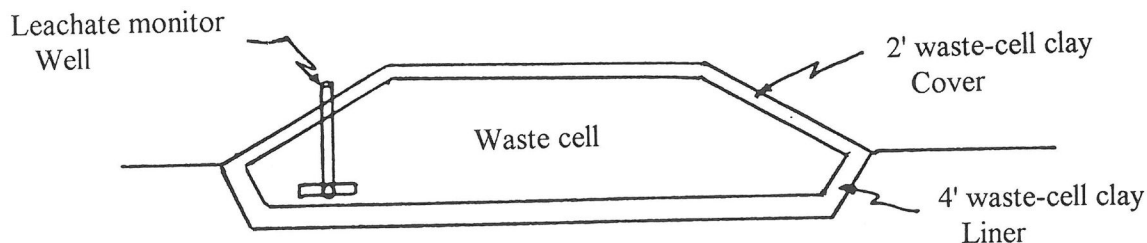


Figure 1. The initial proposal for waste disposal at the West End Chicago site, circa 1982.

Table 1. National siting criteria for shallow-land burial of low-level radioactive waste (U.S. Nuclear Regulatory Commission, 1981) as printed by Hawley, J.W. and Longmire, P.A., Site Characterization and Selection, in C.C. Reith and B.M. Thomson, *Deserts as Dumps? The disposal of Hazardous Materials in Arid Ecosystems*, Univ. of New Mexico Press, 1992, p. 76.

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1. The disposal site shall be capable of being characterized, modeled, analyzed, and monitored.
 2. Within the region or state where the facility is to be located, a disposal site should be selected so that projected population growth and future developments are not likely to affect the ability of the disposal facility to meet performance objectives.
 3. Areas must be avoided having economically significant natural resources that, if exploited, would result in failure to meet the performance objective.
 4. The disposal site must be generally well drained and free of areas of flooding or frequent ponding. Waste disposal shall not take place in a 100-year flood plain, coastal high-hazard area, or wetland.
 5. Upstream drainage areas must be minimized to decrease the amount of runoff which could erode or inundate waste disposal units.
 6. The disposal site must provide sufficient depth to the water table that groundwater intrusion, perennial or otherwise, into the waste will not occur.
 7. Any groundwater discharge to the surface within the disposal site must not originate within the hydrogeologic unit used for disposal.
 8. Areas must be avoided where tectonic process such as faulting, folding, seismic activity, or volcanism may occur with such frequency and extent to significantly affect the ability of the disposal site to meet performance objectives or may preclude defensible modeling and prediction of long-term impacts.
 9. Areas must be avoided where surface geologic processes such as mass wasting, erosion, slumping, land sliding, or weathering occur with such frequency and extent to significantly affect the ability of the disposal site to meet performance objectives or may preclude defensible modeling and prediction of long-term impacts.
 10. The disposal site must not be located where nearby facilities or activities could adversely impact the ability of the site to meet performance objectives or significantly mask the environmental monitoring program.
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Table 2. Performance objectives, waste-management assumptions, and recommended siting criteria from K.L. Falconer, L.C. Hull, and S.A. Mizell (1982) Site selection criteria for shallow land burial for low-level radioactive waste, in R.G. Post, Waste Management '82, Volume 2. Low-level waste: Proceedings of the Symposium on Waste Management at Tucson, Arizona, Arizona Board of Regents, and as reprinted in C.C. Reith and B.M. Thomson, Deserts as Dumps? The disposal of Hazardous Materials in Arid Ecosystems, Univ. of New Mexico Press, 1992, p. 77-8.

Performance Objectives

1. The annual dose from radionuclides released from any shallow land burial site to persons outside the site boundary shall not exceed 25 mrem/yr-thyroid, 25 mrem/yr-any organ, for a performance period of 500 years.
2. Waste shall not be disposed of in a shallow land burial site that would result in an unacceptable dose to an inadvertent intruder after an institutional control period of 100 years has ended.

Assumptions about Waste Management Systems

1. The site will be selected, designed, operated, and closed to meet performance objectives. Zero release is not achievable.
2. Performance objectives can be met by utilizing both natural and engineered barriers.
3. After the institutional control period, the site will be suitable for normal surface use but will not be designed to prevent human excavations into the waste.
4. Waste form will not jeopardize site performance.

Site Selection Criteria

1. *The site should be of sufficient area and depth to accommodate the projected volume of waste and a three-dimensional buffer zone.*

To meet site performance objectives for low-level radioactive waste disposal, the site and its operation must not limit the activity of humans beyond site boundaries. A three-dimensional buffer zone will allow waste attenuation within the site boundary such that performance objectives are met. The essential information required to determine outer boundaries of the site (i.e. the buffer zone) includes the rate of change of radionuclide concentration as a function of distance from the disposal facility along all migration pathways and the concentration and quantity of radionuclides in the waste source. The depth to which the buffer zone extends depends on the hydrologic, geologic, and climatic setting of the disposal facility and whether waste is buried in unsaturated or saturated materials.

In environments where infiltration does not reach the zone of saturation, such as areas where evapotranspiration plus runoff equal or exceed precipitation, solutes dissolved from upper soil horizons are deposited in a zone of accumulation. Material leached from the waste would be deposited in the zone of accumulation and would not reach the saturated zone. Between the zone of accumulation and the capillary fringe is a zone of low geochemical activity. The buffer zone boundary could be in this inactive zone if sufficient leeway is allowed for potential climatic changes or enhanced infiltration through the disposal trenches.

In very arid climates, little or no water is available for leaching, and a thick zone of low geochemical activity separates buried waste from an underlying saturated zone. This environment would present a minimal probability of release by groundwater pathways, and the lower buffer zone boundary could be placed at a moderate distance below the disposal horizon.

2. *The site should allow waste to be buried either completely above or below the transition zone between the unsaturated and saturated zones.*

The reliability of performance prediction may be significantly decreased by burial of waste in the transition zone and greater radionuclide release rates may result from the increased geochemical activity associated with this zone. To determine compliance with this criterion, it is necessary to examine the water table elevation, the range of both seasonal and long-term water table elevation, the range of both seasonal and long-term water table fluctuations, height of the capillary fringe, thickness of excavatable material, and, if waste is buried below the transition zone, the hydraulic characteristics of earth materials in the saturated zone.

3. *The site should be located where flooding will not jeopardize performance.*

Where burial occurs above the water table, flood waters can transport waste material and/or saturate the waste, increasing leachate formation and accelerating subsurface water flow. Flooding can also interfere with site operations irrespective of the zone of burial. Locating burial sites outside areas that require extensive engineered protection will ensure that no increase in the probability of flooding occurs during the performance period of the site because of failure of engineered barriers.

4. *The site should be located where erosion will not jeopardize performance.*

During the required performance period of the site, erosion by wind and water must not cause intrusion on the buffer zone and/or waste cover such that it (a) uncovers the waste, (b) increases surface radiation levels above regulatory limits, and/or (c) significantly shortens radionuclide release pathways. Waste that is uncovered is susceptible to transport from the site, but erosion does not have to uncover the waste to shorten migration pathways significantly. During closure, certain engineered structures, such as trench caps, will likely be emplaced to improve waste containment. Erosion of these emplaced structures could decrease the performance capabilities of the site. Allowances for predicted rates of erosion during the site performance period should be incorporated into site design, operating, and closure criteria.

Plant cover and moisture availability are the most important factors governing the rate of erosion by both wind and water. Where average annual precipitation is very low, natural vegetation may be sparse or absent, allowing high wind erosion rates and high water erosion rates whenever precipitation does occur.

5. *The site should be located in areas where hydrogeologic conditions allow reliable performance prediction.*

Confident characterization of the hydrogeologic system in which a waste disposal site is located enables determination of potential migration pathways, estimation of radioactive contaminant movement rates in the subsurface environment, and design of a monitor network to collect data that can be used to confirm performance predictions of radionuclide transport. Major hydrologic characteristic of the site that must be examined include: subsurface geology, hydrologic budget, direction and magnitude of ground water flow, permeability type and diffusion properties of the system.

6. *The site should be located where geologic hazards will not jeopardize performance.*

Significant land disturbances may destroy site integrity and increase the likelihood of radionuclides entering the biosphere. In addition, site hydrology may be altered to the extent that performance predictions are no longer applicable. Specific geologic events that must be considered include earth movement associated with seismic activity, mass movement, land subsidence, and volcanic activity. The results of these events in the geologic past may so complicate the hydrogeologic system that predictions of site performance cannot be confidently obtained.

7. *The site should be selected with consideration given to those characteristics of earth materials and water chemistry that favor increased residence times and/or attenuation of radionuclide concentrations within site boundaries.*

Leachate migrating from buried wastes may carry radionuclides and other contaminants picked up from the waste. Showing the movement of contaminants relative to the movement of water will provide more time for radioactive decay to decrease radionuclide concentrations. Properties of earth materials and water chemistry that favor the removal of radionuclides from solution by sorption or precipitation and that favor retention on or in solid phases, will retard the movement of radionuclides. Nuclide concentration will decline more rapidly with distance from the waste if geochemical processes actively remove radionuclides from leachate than if only hydrodynamic dispersion is acting.

8. *The site should be selected with consideration given to current and projected population distributions.*

The minimum distance a site can be located from the population cluster must be determined by considering the size of the population and the effects of potential accidental and chronic radiation released during operations. A site located close to population centers could interfere with their expansion, as well as increase the likelihood of human intrusion into the waste after institutional control has ended.

9. *The site should be selected with consideration given to current and projected land use and resource development.*

Site selection must represent a balanced choice in land use, in that siting represents a commitment in land use to future generations. Historical, current, and potential land uses at the site and the adjacent areas should be prime considerations in complying with this criterion. Land uses which represent a higher priority in comparison to low-level waste disposal should be evaluated.

10. *To the extent consistent with other criteria, the site should be selected with consideration given to location of waste generation, access to all-weather highway and rail routes, and access utilities.*

A certain risk exists from the transport of radioactive waste from points of generation to final disposal. This risk is a function of the waste form, nuclide content, vehicle safety, transportation systems, and distance traveled. By considering major points of waste generation and transportation routes in site selection, this risk can be reduced. Locating a site with regard to waste generators and transportation systems also minimizes the cost of land disposal. Additional economic factors that can be controlled through site selection include access to utilities, materials for site construction, operation and closure, and public services.

11. *The site should be selected consistent with federal laws and regulations.*

Federal laws that a disposal site must comply with include but are not limited to: Clean Air Act (PL 95-95), Federal Water Pollution Control Act (PL 95-217), Safe Drinking Water Act (PL 93-523), National Environmental Policy Act (PL 91-190).

12. *The site should not be located within areas that are protected from such use by federal laws and regulations.*

Federal laws which preclude, by intent, the selection of low-level waste disposal sites within the boundaries of areas protected under them include but are not limited to: Wilderness Act of 1964 (PL 88-577), Wild and Scenic Rivers Act (PL 90-542), Endangered Species Act of 1973 (PL 93-204), National Wildlife Refuge Act of 1966 (PL 89-669), Laws establishing National Parks, Historic Properties-Preservation (PL 89-665), Archeological and Historical Preservations Act of 1974 (PL 93-291).

NOTES TO THE INSTRUCTOR

The concept of this laboratory originated in 1993 from the need to develop an environmental geology course. The overall objective of the course was to teach a broad understanding of earth processes and systems so that students could become informed consumers of scientific information. One portion of this course required an applied or environmental mineralogy component, with sufficient introductory material that a consistent background could be provided even if the course is taught by different instructors. Also, the laboratory needed to be simple, relatively inexpensive, easy to maintain and set up, capable of being completed within a two-hour period, and comprehensible for students with only minimal backgrounds in chemistry, since the course was not intended just for geology majors. Although this exercise was originally designed for an environmental geology course, it is applicable to many courses, including hydrology, mineralogy, sedimentology, geomorphology, physical geology, etc.

The resulting environmental mineralogy laboratory illustrates several important general mineralogical concepts. Although not always explicitly stated in the laboratory text, these concepts include cation sites and cation exchange, solid solution, charge neutrality of the chemical constituents in phases, and the effect of chemical composition on the physical properties of phases. Other concepts are more appropriate for clay mineralogy, such as the effect of salts on the behavior of clay swelling, plastic behavior of clays, and permeability.

Although this laboratory exercise is self-contained, it was not meant to stand alone. The laboratory leads not only to possible discussions of the scientific concepts given above, but also of how natural materials may be used to isolate or remediate chemical or nuclear waste. For example, courses may include discussion involving how to isolate low-level radioactive waste by using a clay containment system; we use an example near Chicago where low-level radioactive waste was to be sited within city limits. The discussion involves background information and past legal action, site conditions, a design of a proposed containment cell, national siting criteria, proposed performance objectives, and about 25 topics and questions to explore. This discussion is included here also, although with changes to names and details to protect the identity of the participants.

Special comments on the experiments and experimental procedures. It is noteworthy that the montmorillonite used in this laboratory must be of high purity. For example, cat litter and othersimilar sources are generally not of sufficient quality for these experiments. We use a high-purity montmorillonite¹ available commercially, but other sources may provide material of high quality.

Part II of the laboratory considers the flow rate of water and Na-rich brines through a column of a montmorillonite + sand mixture. The times required for flow (Questions 8, 9 and 10) are dependent on the particle size of the sand used, the amount of montmorillonite added to the sand, and the quality of the montmorillonite used in the experiments. Pore sizes in the sand must be sufficiently small to trap some of the montmorillonite and to allow the montmorillonite to seal upon expanding. A sand with grain sizes ranging up to fine-medium has worked well, and a poorly sorted sand may be better than a well sorted sand. Also, Question 6 of Part II must be modified for the appropriate amount of added montmorillonite. The instructor should test the mixture so that the first experiment in which water drains through the column takes about 3-4 minutes (Question 10, Part II).

¹ unmodified Supercol[®], available from American Colloid Company, 1500 W. Shure Dr., Arlington Heights, IL 60004, USA. A gallon of unmodified Supercol[®] will last for years. American Colloid has provided these quantities free of charge as a service to the educational community. Please offer to purchase the material, however.

An important point in Question 7 of Part II is that montmorillonite must not form a layer on the top surface of the column. Clay is an effective sealant, and if a clay layer is allowed to form, water is impeded from flowing through the column. Decanting excess water above the column often prevents a clay layer from forming to seal the column surface. Likewise, to prevent clay concentrations from forming, it is imperative that the student thoroughly mix the clay into the sand (for Question 6, Part II).

Sand obtained commercially may already contain clay. To check for clay material, place some sand in a large beaker with water and stir. If the resulting water appears cloudy, the sand contains a clay fraction, which must be washed from the sand before proceeding with the experiments. Successive stirring of the sand with clean water will remove the clay.

Anticipated results. Part I illustrates how cation exchange may affect the physical properties of the clay. Cation exchange takes place almost immediately upon stirring the montmorillonite in the saturated solutions of NaCl, MgCl₂, or CaCl₂. The wait time of 5 minutes is for the purpose of settling. The Na-exchanged clay, which contains H₂O in the interlayer also, does not settle to the same extent as the other exchanged montmorillonites. As more Cl is removed by washing, the Na exchanged montmorillonite will disperse. This effect may be apparent within one or two washings. If the clay is washed sufficiently (four or five times), however, the use of an ultrahigh speed centrifuge will be required to bring the clay to the bottom of a container.

Part II examines the property of permeability through a sand column vs composition of the montmorillonite. Parallel experiments are done to isolate the effect of permeability of the sand column using pure water and then NaCl saturated solution, followed by the same fluids with a sand + Ca-exchanged montmorillonite column. The NaCl saturated solution (Part II, Question 4) takes substantially longer to flow through the sand column than pure water, presumably because of its different ability to wet the sand grains.

The student (Question 9, Part II) introduces NaCl saturated fluid into the column containing Ca exchanged montmorillonite, and this sets up a Na exchange. However, because of the Cl present, the (now Na exchanged) montmorillonite does not disperse. Adding pure water in Question 10 washes the Cl (and excess Na and other cations having been exchanged from the clay) from the sand, thereby causing dispersion which closes the pore throats of the sand. Question 10 suggests that three washings are necessary, but this may vary and it may only be necessary to do two washings (less commonly, four washings). Variations in the number of needed washings are common, since the flow of water in the column cannot be controlled. In any case, if the students are waiting around watching a diminishing flow rate, then the point has been made.

Note that it takes only a small amount of montmorillonite to affect a considerable amount of sand. Also, brines passing through sands with some clay, followed by fresh water, clearly can greatly affect the permeability of the sands. Not only is this an important consideration in remediation work in the environmental industry, but it is also important in the petroleum industry and in the understanding of quick clays, stability problems, and many other engineering-related problems.

Question 11, which involves the introduction of methylene blue to the column, illustrates the ability of montmorillonite (+ sand) to adsorb other materials, and thus it acts as a "filter". The blue color is readily adsorbed in the top couple of centimeters of the column. Methylene blue is an organic molecule with an associated positive charge, and it is adsorbed quickly by the clay. An alternative experiment, in case class time is a concern, is to add the methylene blue directly to a beaker containing montmorillonite + water. The clay will adsorb the dye very quickly.

Additional classroom experiment. A short class demonstration to illustrate clay dispersion and swelling behavior are not included in this exercise, but it is appropriate for an introduction to the properties of clay minerals. Clay dispersion is best illustrated over several days so it is best to set up this demonstration in one class period and then to return to it at intervals up to a week.

Take two 150 ml. glass beakers and fill each about 3/4 with water. In one beaker add about 3 tablespoons of sand or soil (provided the soil does not have a significant clay component). In the other beaker, add a similar amount of montmorillonite (use the same montmorillonite as in the laboratory exercise). Stir the soil/water mix, but it is not necessary to stir the montmorillonite/water mix (if there is a time constraint, stir the montmorillonite very gently for a brief time). Allow both beakers to stand for two or more days. Larger beakers can be used with greater amounts of clay and water. Unlike the soil/water mix where the soil settles to the bottom of the beaker, the clay particles will disperse throughout the beaker of water. Materials generally do not behave this way! If the water is allowed to dry from the beaker with montmorillonite, the result will be a mass of hardened clay (clay + interlayer water) many times the volume of the initial 3 tablespoons.

SUGGESTIONS FOR THE LOW LEVEL RADIOACTIVE WASTE DISPOSAL DISCUSSION

The class may be divided into three groups, advocates for Nosean Mining Company, advocates for the citizens of the City of West End Chicago, and advocates for the NRC. The discussion leader can be the (impartial) judge. As judge, you may ask questions, but do not expect to render a "decision". The discussion should be considered "open-ended".

Topics and questions to explore:

Is there anything conceptually incongruous about disposal-site use for recreational use? Could recreational use actually accelerate deterioration of the cell? If snowmobile or motorcycle use are allowed, how could this affect the cell cover?

How may freezing and thawing affect cell cover integrity? How may drying and wetting affect the cell cover?

What may be the effect of borrowing animals, such as badgers, have on the integrity of the site? Consider both the effect on the cell cap and in the interior of the cell (void spaces). Does this suggest that such a site should be left unmonitored?

What are the negative effects of vegetation with extensive root systems? Are there any positive effects? Should vegetation grow in the disposal site without monitoring? Are there any effects from decomposing organic matter?

If monitoring is a wise idea, for how long should it be done? What are the criteria set forth by the NRC.

What is the "bath tub" effect? Does the engineering of this cell promote or lessen the possibility of the bath tub effect? What must be done to prevent the effect?

How would the designers of the cell determine if the cell fails? Do the leachate wells presently suggested test for failure? How would you design a cell to test for possible failure?

How may water run-off possibly affect the cell cover? How does erosion (e.g., wind, water, ice, etc.) in the Chicago area proceed? What will be the impact of raindrops during

intense summer storms be on an unprotected clay cover? How may an extensive drought affect the cell integrity? Describe gully erosion, mass movement.

What site characteristics are at odds with the criteria set forth by the NRC? Discuss the criteria set forth regarding population, potential land use, and potential population increase.

What may be the effect of possible air pollution found in the Chicago area, such as acid rain (sulfuric acids)?

Although the cell contents will be artificially compacted during emplacement, how may additional natural compaction affect the cell integrity?

Discuss more ideal locations and climates for waste disposal. What would be considered "ideal" to you? What criteria did you use to decide on an ideal location?

What are the aesthetic objections for the West End Chicago site that might be offered by the citizens of the City and State? If the current siting proceeds, will the objectives of the City and State be met?

Should there be any criteria regarding slopes on the cell? How may this prove important?

For more advanced discussions:

Have the students design a waste disposal cell.

Discuss ways that geology may be used in the design of a "natural site" depository in conjunction with a well designed cell or cover.

How would low level waste disposal differ from high level waste disposal?

How would low level waste disposal differ from hazardous chemical waste disposal?

Discuss the rationale behind using a clay cover--Is such a cover to prevent all water from entering the cell or to limit water? How should the cell character differ or be related to liner characteristics?

What are slurry trenches and how may their use limit seepage? Discuss the purpose of redundant liners and leak detection systems.

Discuss possible biointrusion barriers to prevent burrowing animals or penetration of roots. Also consider the design of drains, swales, aprons, and infiltration barriers.

How would you design a marker to serve as a warning to future generations? Remember that the curses of the pharaohs were not particularly effective in stopping thieves and English language markers may be equally ineffective. Remember also that the limestone blocks on the pyramids, which represented quality building material, was stripped from the pyramids shortly after they were built.

What sort of performance assessments should be made on the site?

*** ERRATA ***

Corrections to Guggenheim, S. (1997) Introduction to the properties of clay minerals. *Teaching Mineralogy*, Brady, J.B., Mogk, D.W., and Perkins, D., III, Eds., Mineralogical Society of America, Washington, 371-388.

replace paragraphs 4 and 5 on p. 375 with:

Clay minerals may be made to disperse or flocculate in water. "Dispersed" clay is the case where individual particles are separate and remain in suspension in the fluid. "Flocculation" is where the particles aggregate to form clumps or "flocs" (Figure 6). As the clay flocculates, the flocs fall to the bottom of the glass or beaker.

Colloid chemists are not at all certain about the details of why dispersion and flocculation occur, although a basic understanding is known. For the purposes of this laboratory, it is sufficient to recognize that at low salt concentrations, dispersion generally occurs. Interparticle attraction (flocculation) generally occurs at higher salt concentrations. Thus, a cation exchanged montmorillonite in a salt solution may be made to disperse by washing in pure water to remove the salt. Usually, it takes several washings (sometimes up to six) to remove the salt sufficiently. Depending on what experiments or processes are planned, sometimes it is more convenient to work with either a dispersed or a flocculated clay.

replace Figure 6 with:

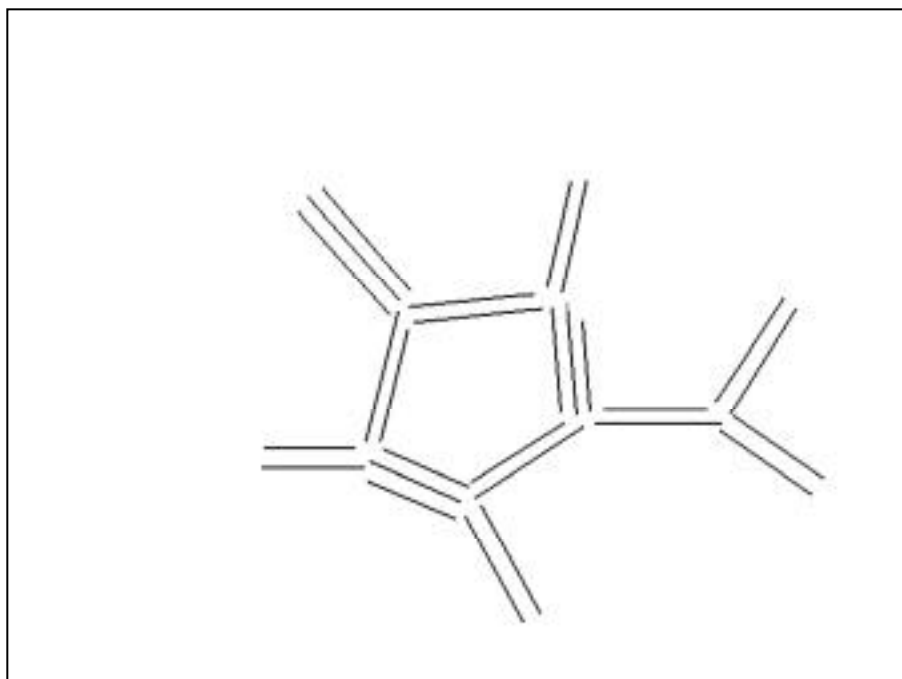


Figure 6. Schematic showing flocs may form by edge-to-edge attraction.

- p. 376, Part I, step 3, line 2: replace "chloride (Cl)" with "salt"
- p. 376, Part I, step 3, line 3: replace "Cl ions" with "salt"
- p. 376, Part I, step 3c. line 3: replace "No" with "Now"
- p. 385, footnote, line 1: replace "Supercol" with "Supergel"
- p. 385, footnote, line 2: replace "Supercol" with "Supergel"
- p. 386, line 15: replace "Cl" with "salt"
- p. 386, line 26: replace "Cl" with "salt"
- p. 386, line 28: replace "Cl" with "salt"

MINERAL SEPARATION AND PROVENANCE LAB EXERCISE

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INTRODUCTION

This lab exercise has three main objectives: 1) to help students learn to identify mineral grains under the binocular microscope; 2) to demonstrate differences in density and magnetic properties among minerals; 3) to see how a river's sand-sized sediment fraction reflects its source.

PROBLEM

Students will examine mineral separates from sand samples collected from a number of rivers each of which drains a slightly different geologic terrane. Differences in mineralogic composition and mineral abundance will be used to suggest different provenance for each of the sand samples. These sand samples may be treated as unknowns or the students may be informed of where the sand was sampled. At the end of the mineral separations and binocular microscope identification, the students may be allowed to consult geologic maps of the regions sampled to aid in their provenance determination.

Sand samples from a minimum of the three rivers will be provided. The number of samples examined should be proportional to class size with the students divided into groups of three to four.

PROCEDURE

Sieving

All pebbles and grains >20 mesh must be sieved out. If the sand sample contains significant clay, this must also be removed either by using a flotation table such as a Wilfley or a Gemini gold table or by "gold-panning" the sample. "Gold-panning" involves using either a gold pan or an aluminum baking dish. The sample is placed in the container and wet thoroughly with running water. The wet sample is then agitated to suspend the clay fraction which is decanted into some kind of sediment trap. The clay fraction must be removed because it will make the heavy liquid separation extremely difficult and unsuccessful.

Separations

The sieved sand samples will be subjected to a series of mineral separation techniques which will separate the less dense (<2.9 g/cc) from the more dense (>2.9 g/cc) minerals (Klein and Hurlbut, 1993) and the magnetic from non-magnetic minerals (Rosenblum, 1953). This will permit easier identification and estimation of percentages.

The samples will be weighed at the start of the exercise and at various points as indicated during the separation. This helps determine how much sample is lost during processing. The final report will include the sample weights, estimation of percentages of minerals at different stages during the process, and a provenance determination for the sand samples which may be verified by examination of a geologic map.

MINERAL SEPARATIONS

Before beginning mineral separations, sand samples must be weighed. All data can be recorded on the attached worksheet.

Heavy Liquids

We will be using sodium polytungstate (SPT) which has a specific gravity of 2.89. It is non-toxic for inhalation and skin contact so it can be used without a fume hood and protective clothing. It is water-soluble. Please wash your hands after use to remove any residue. SPT is **VERY EXPENSIVE** (~\$90/lb.) so be careful to recover all of the solution possible and avoid spilling it.

Sodium polytungstate (SPT) evaporates easily so do not leave the bottle uncovered. The heavy liquid separations should be done quickly and efficiently to avoid excessive evaporation of the SPT. All separates need to be rinsed thoroughly, several times with water, preferably distilled water. If rinsing is not carefully done, the sodium polytungstate will dry into a hard mass on the sand grains and prohibit further processing.

Directions.

1. **After making sure that the stopcock is closed**, pour SPT into a large separatory funnel in an amount proportional to sample size. Mark the funnel with the sample number.
2. Add a sand sample and stir with stirring rod until all sand is wet thoroughly.
3. Allow the heavy minerals (>2.9 g/cc) to sink. This should take **no longer** than 10 minutes.
4. With help, draw off the heavy minerals into a funnel lined with a filter paper and collect SPT in an Erlenmeyer flask. Because of the high viscosity of SPT, a vacuum pump can be used to help speed up the draining of the filter paper. Transfer the funnel containing the heavy mineral separate to a second Erlenmeyer flask and rinse several times with water, preferably distilled, from a squeeze bottle.
5. Remove the heavy fraction on the filter paper after rinsing and dry on a watch glass. An acetone rinse will facilitate quicker drying.
6. Repeat the drawing-off, rinsing and drying procedures for the light mineral fraction (<2.9 g/cc).
7. Examine the two fractions (light and heavy) under a microscope and determine the mineral composition and percentages for each fraction.
8. Weigh each fraction to determine amount of sample lost in processing.
9. Repeat the heavy liquid separation on the other sand samples.

Magnetic Separation

This mineral separation step will use just the heavy mineral fraction. Here, separation of the magnetic from non-magnetic minerals is accomplished using a Frantz isodynamic separator.

1. First, to remove the extremely magnetic minerals, such as magnetite, from the heavy mineral fraction we will use a free-fall magnetic separation. Attach a paper cone to the front of the Frantz which has had its magnet rotated into a vertical position. Place a beaker or pan underneath the Frantz and turn magnet current to the maximum (~1.6A).
2. Pour sample through the paper cone. The magnetic minerals will stick to it. Non-magnetic minerals will “fall” through into the beaker. Remove the beaker of non-magnetic minerals when all of the sample has gone through the funnel.
3. Place another beaker underneath the funnel and turn off magnet current. The magnetic fraction will fall into beaker. Save and examine under binocular microscope. Note the mineral compositions and percentages.
4. Examine the non-magnetic minerals under a binocular microscope. Note the mineral compositions and estimate percentages.

Now, the Frantz is changed in orientation so that it is tilted 10° to the back (dial viewed when looking at front of Frantz) and 25° down toward the front (dial viewed when looking at magnet end on). The current will be increased incrementally and fractions collected at different current settings representing differences in magnetic susceptibility. Place all magnetic fractions and the final non-magnetic fraction in separate vials labeled according to amp setting. Examine all fractions, magnetic and non-magnetic under binocular microscope and determine mineral composition and estimate percentages.

5. First, place the non-magnetic free-fall sample in the Frantz cup making sure it is closed, turn up current to 0.3A; and turn on vibrating mechanism. Open the cup enough to allow grains to vibrate freely down the trough through the magnet and into the collection cups.
6. Collect magnetic and non-magnetic fractions. Remember the magnetic fraction is always the one pulled uphill, i.e., the one in the cup at the highest angle, closest to the analyst.
7. Always place the non-magnetic fraction back in the Frantz cup. Repeat the non-magnetic and magnetic separation at 0.5A, 0.8A, and 1.2A.
8. Weigh all fractions, magnetic and non-magnetic, for each sand sample to determine total loss during separation.
9. Use Table 1 to identify the minerals present in each magnetic fraction.

ADVICE TO THE INSTRUCTOR

This lab is designed for small mineralogy lab sections with 15 students being a reasonable upper limit. I have the students work in groups of three or four so that they can all have a task in each step of the separation process. With larger groups, some students cannot actively participate in all separation steps and may lose interest.

It is also necessary to have some mineral separation equipment available. My research specialty is fission-track dating so I have state-of-the-art facilities. Most large research universities may be similarly equipped. Smaller colleges may not have either a Franz magnetic separator or appropriate large separatory funnels. In this case, it is probably not wise to do this lab.

Separatory funnels - Remember sand-sized grains need to pass through the stopcock so use a large (1000 ml) separatory funnel. Do a trial run with the separatory funnels before you choose to do the lab with students. Be sure to take the stopcocks out of the funnels and rinse well immediately after doing the separation otherwise, the stopcock may freeze shut with SPT.

Sodium Polytungstate (STP) - This product, although non-toxic, is more difficult to use than the toxic heavy liquids. As indicated previously, it evaporates extremely quickly and is very viscous. Thorough rinsing of samples and separatory funnels is absolutely necessary! Using a small vacuum pump to help drain the liquid is highly recommended. This will cut the heavy liquid separation time in half and reduce student restlessness.

Sodium Polytungstate (STP), as well as information on recovering STP from its solid form in case of evaporation, can be obtained from the following vendor:

POLY-GEE Sodium Polytungstate (density 2.8 liquid or powder)

Geoliquids, Inc.
15 E. Palatine Rd. Suite 109
Prospect Heights, Illinois 60070
800-827-2411
847-215-0938
847-215-9821 (fax)

Franz Isodynamic Separator - If your department does not have one of these, a separation of the very magnetic minerals (magnetite) can be accomplished with an hand magnet held behind a sheet of paper. If you do have access to a Franz, Table 1 gives the magnetic susceptibilities for common heavy minerals. This will give you an idea of what minerals appear in different fractions with increasing current.

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*These are selected references, and are meant to be a starting point for scholarship on education. There is a wealth of information on instructional materials and methods in journals such as the *Journal of Geoscience Education*, *Journal of Chemical Education*, *Journal of College Science Teaching* and many others.